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RADIATION-INDUCED CHANGES IN EXPLOSIVE MATERIALS

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Picatinny Arsenal
Dover, New Jersey

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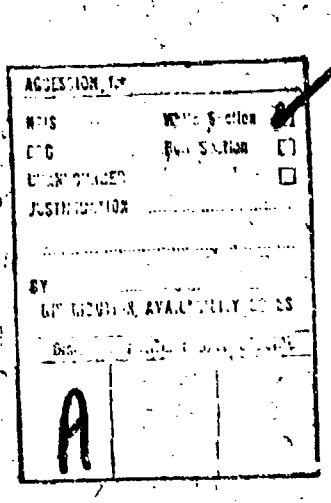

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Picatinny Arsenal Technical Report 4602

RADIATION-INDUCED CHANGES IN EXPLOSIVE MATERIALS

by

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December 1973

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ABSTRACT

A group of eleven explosive materials in powder and pellet form were subjected to Co^{60} gamma radiation and the results are tabulated and discussed. The explosives were studied using weight loss, dimensional change, vacuum stability, DTA, TGA, infrared spectra, melting point, impact sensitivity, explosion temperature and rates of detonation as a function of total gamma exposure up to and including levels of 10^9 R. Based on this work, a damage threshold as a function of total gamma dose was determined for each material. The results indicate that the capability of the explosives studied to withstand Co^{60} gamma radiation decreases in the following order:

TACOT $\geq$ TATB $\geq$ DATB > HMX $\geq$ Tetryl $\geq$ TNB $\geq$ TNT > RDX $\geq$ PETN >

NGu > BaN_6.

INTRODUCTION

From 1966 to 1971 a program was conducted at Picatinny Arsenal to investigate and determine the effects of gamma radiation on several explosive materials. The purpose of the program was to determine the capability of the explosive materials to withstand an ionizing radiation environment and to determine their radiation exposure limits. This program was conducted in conjunction with an Air Force program studying the effects of gamma radiation on selected fluoroexplosives.[1] This program also was an outgrowth of a similar study in which a large number of reactive materials were subjected to a nuclear reactor radiation environment in order to determine their radiation resistance.[2,3]

The following explosives were studied:

1. BaN_6 (barium azide)
2. DATB (diaminotrinitrobenzene)
3. HMX (cyclotetramethylenetetranitramine)
4. NGu (nitroguanidine)
5. PETN (penetaerythritol tetranitrate)
6. RDX (cyclotrimethylenetrinitramine)
7. TACOT (tetranitrodibenzotetraazopentalene)
8. TATB (triaminotrinitrobenzene)
9. Tetryl (trinitrophenylethylnitramine)
10. TNB (1,3,5 trinitrobenzene)
11. TNT (2,4,6 trinitrotoluene)

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A group of eleven explosive materials in powder and pellet form were subjected to Co^{60} gamma radiation and the results are tabulated and discussed. The explosives were studied using weight loss, dimensional change, vacuum stability, DTA, TCA, infrared spectra, melting point, impact sensitivity, explosion temperature and rates of detonation as a function of total gamma exposure up to and including levels of 10^9 R. Based on this work, a damage threshold as a function of total gamma dose was determined for each material. The results indicate that the capability of the explosives studied to withstand Co^{60} gamma radiation decreases in the following order:

TACOT $\geq$ TATB $\geq$ DATB > HMX $\geq$ Tetryl $\geq$ TNB $\geq$ TNT > RDX $\geq$ PETN > NGu > BaN_6.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gamma Radiation						
Radiation Effects in Explosives						
Weight Loss						
Dimensional Charge						
Vacuum Stability						
Differential Thermal Analysis						
Thermogravimetric Analysis						
Infrared Spectra						
Melting Point						
Impact Sensitivity						
Explosion Temperature						
Detonation Velocity						
Barium Azide						
DATB						
HMX						
Nitroguanidine						
PETN						
RDX						
TACOT						
TATB						
Tetryl						
TNB						
TNT						

RADIATION ENVIRONMENT

The effects of gamma radiation on the explosive materials were studied using Co^{60} radiation consisting of 1.173 Mev and 1.332 Mev gamma rays. Since these two groups are emitted in equal quantities, the energy is usually reported as 1.25 Mev, the average. Because the gamma ray energy is in the intermediate energy range, the major radiation damage to the organic materials studied in this program was induced by ionization caused by the predominant Compton effect.

The 10,000 curie Co^{60} radiation source used is located at Picatinny Arsenal. The radiation intensities were determined by the LiF thermoluminescent dosimetry method. The dose rates in this study ranged from 6.4 to 9.2 x 10^5 R/hr while the total exposures were from 10^7R to over 10^9R. In this report, the unit chosen to express the exposure is the roentgen (R). The energy conversion factor for absorbed dose are:

1R (of dry air) = 87.7 ergs (absorbed)/g (C)

1.14R = 100 ergs/g (C) = 1 rad

EXPERIMENTAL PROCEDURE

The irradiated explosive materials were in two forms: powder (granular) and pellets pressed from the powder. The cylindrical pellets, pressed without binders, were 1/2-inch thick and about 3/4-inch long.

For irradiating the explosive powders, about 1.5 grams of explosive were placed in a quartz vial (50 mm long, 9 mm I.D. and 1 mm wall thickness) and four vials were placed in a 12-inch long aluminum tube with a 1/2-inch O.D. and a 0.22-inch wall thickness. The vials were centered in the tube by means of a 3/8-inch diameter aluminum or glass rod. The bottom of the tube was closed by using glass wool as a plug. This assembly was then inserted into a stainless steel containment capsule. This capsule was constructed from 1 1/2-inch-diameter, 12-inch-long No. 316 stainless steel pipe with a 0.145-inch wall. The bottom end of the capsule was closed by a welded stainless steel pipe end cap. The top section which is welded to the pipe consists of an adapter with a threaded hole into which a 3/4-inch O.D.

threaded stainless steel plug is screwed. The plug was reamed out so that when the aluminum tube with the powder samples is inserted into the capsule, the screwing-in of the plug automatically centers the tube. Figure 1 illustrates the containment capsule, the aluminum tube, and the quartz vials with powder prior to assembly. The overall length of the capsule is 14 inches.

The purpose of the capsule was to serve as a containment vessel to ensure that the Co^{60} source would not be damaged in any way if any of the explosive detonated during irradiation. This capsule had been tested to contain a detonation produced by 20 grams of pressed HMX.[1]

To irradiate the 1/2-inch diameter pellets a 5/8-inch O.D. aluminum tube with a 0.035-inch wall was used. In this 12-inch tube, seven pellets were placed, the height being governed by a 1/2-inch diameter glass or aluminum rod. This in turn was kept in place by a glass wool plug at the bottom of the aluminum tube. Because the amount of explosive used was larger, the containment capsule for the pellets had to be thicker walled than the capsule for the explosive powder. Thus, while otherwise similar to the powder-containing capsule, the capsule for the explosive pellets was designed to have 0.200-inch-thick walls instead of the 0.145-inch walls used for the powder-containing capsule. This capsule had been tested to contain the detonation produced by 50 grams of pressed HMX.[1] These capsules have been used for gamma irradiations and also as shipping containers for explosive materials for the past seven years without any incidents.

The effects of radiation on the listed explosives were determined by measuring changes in the physical, chemical and explosive characteristics of these compounds before and after irradiation using a variety of standard laboratory tests:

a. Thermal Stability

    1. Vacuum stability

    2. Weight loss and dimensional charge

    3. Differential thermal analyses (DTA)

    4. Thermogravimetric analysis (TGA)

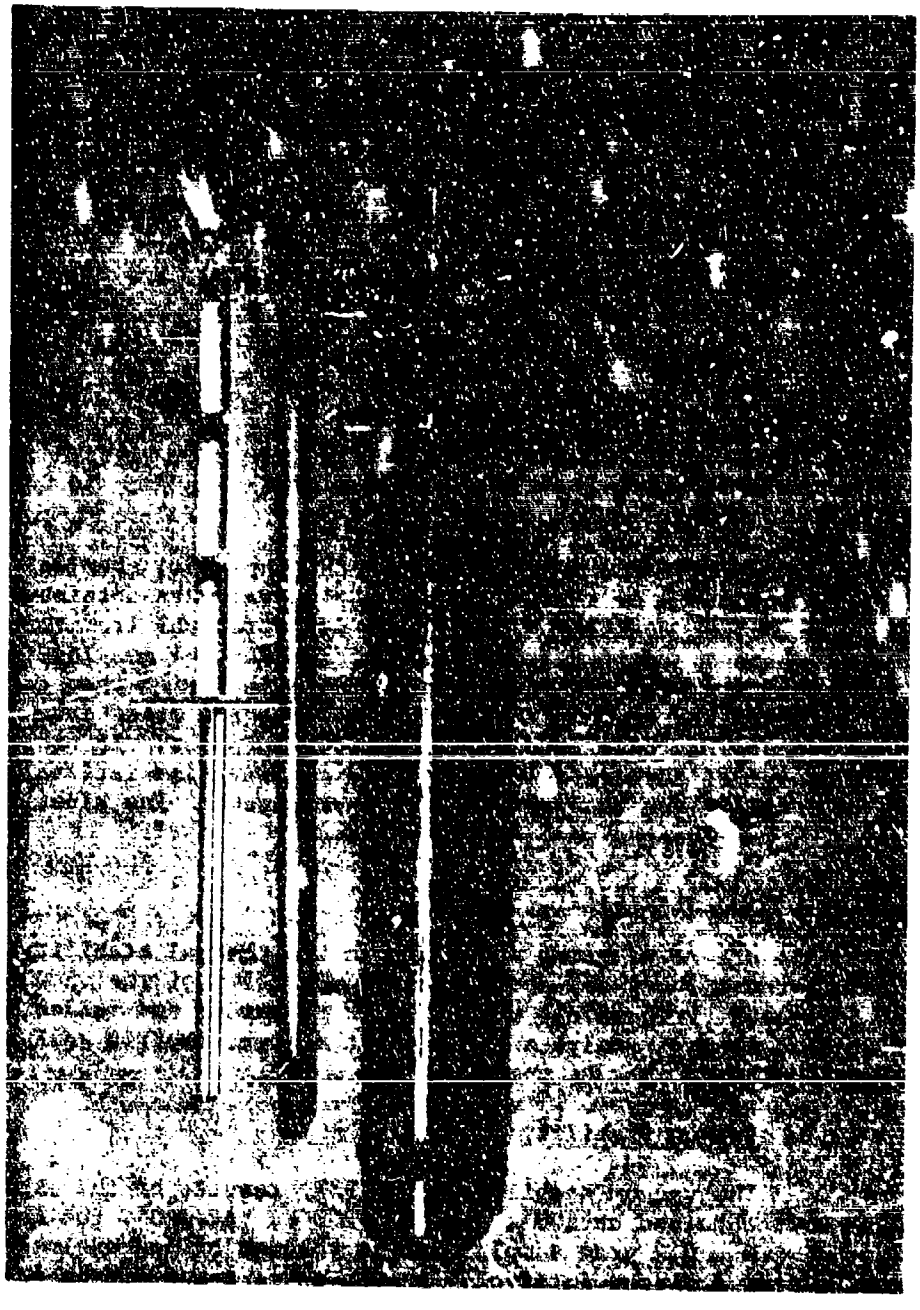

FIGURE 1 Containment Capsule Assembly for Gamma Irradiation of Explosive Powder Sample

b. Purity

1. Melting points and color change

2. Infrared spectra (IR)

c. Sensitivity

1. Impac

2. Explosive temperature

d. Explosive performance

1. Detonation velocity

The majority of the measurements of the physical, chemical and explosive properties of the irradiated explosives were obtained soon after irradiation, normally within hours after removal from the radiation chamber. Most of the values of the control samples (unirradiated materials) were determined during the period when the irradiated explosives were in the radiation chamber. Other data in the open literature was also used for comparison purposes. In other instances some of the tests were repeated after a time interval to confirm if all of the changes noted were permanent. The kinetics involved with the changes were not determined.

a. Thermal Stability

The effect of gamma radiation on the thermal stability of the explosives under study was determined from results of the vacuum stability tests, weight loss measurements on powder and pellet samples, differential thermal analyses (DTA) and thermogravimetric analyses (TGA).

1. Vacuum Stability

The vacuum stability test (VST) results of the explosives studied were obtained at 100°, 120° and 200°C. At 200°C the test was conducted with a 0.2 gram sample and the volumes of gas evolved was measured after a 2 hour interval. At the other temperatures the sample size was 1 gram and the gas evolved was measured after 40 hours. The VST results are listed in Table 1.

TABLE I

EFFECT OF GAMMA RADIATION ON EXPLOSIVES AS SHOWN BY THE VACUUM STABILITY TEST

Explosive	Exposure Rate R/hr.	Total Dose R	Vacuum Stability Test 100°C cc/g/40 hrs.	120°C cc/g/40 hrs.	200°C cc/.2g/2 hrs.
BaN_6	8×10^5	Control	0.39, 0.24[a]		
		1.4×10^7			Deflagrated (1 min)
		1.2×10^8	11+		Deflagrated (1 min)
		1.0×10^9	0.59[a]		
DATB		Control			0.20
	9.2×10^5	1.5×10^7			0.28
		1.3×10^8			0.42
		1.2×10^9			0.90[b]
		4.0×10^9			6.15 (Marginal)
HMX		Control			0.42
	8×10^5	1.3×10^7			1.40
		1.1×10^8			7.09 (Marginal)
		1.0×10^9			Deflagrated (3 min)

TABLE 1 (Continued)

Explosive	Exposure Rate R/hr.	Total Dose R	Vacuum Stability Test 100°C cc/g/40 hrs.	120°C cc/g/40 hrs.	200°C cc/.2g/1 hrs.
NGu		Control		0.47	11+(15 min)
	8×10^5	1.3×10^7		0.49	11+(10 min)
		1.1×10^8		0.71	11+(12 min)
		1.0×10^9	12.15[c]	11+(30 min)	
PETN		Control	0.45	1.54	Deflagrated (8 min)
	6.4×10^5	1.0×10^7	4.43	11+(6 hrs)	Deflagrated (3 min)
		9.0×10^7	11+(30 min)		
RDX		Control	0.09		
	6.4×10^5	1.0×10^7	0.91		Deflagrated (10 min)
		9.0×10^7	11+(16 hrs)		Deflagrated (12 min)
		1.0×10^9	Material Stuck in Vial		
TACOT		Control			0.10
	8.5×10^5	1.4×10^7			0.27
		1.2×10^8			0.14
		1.1×10^9			0.51[b]
		3.7×10^9			2.44

TABLE 1 (Continued)

Explosive	Exposure Rate R/hr.	Total Dose R	Vacuum Stability Test 100°C cc/g/40 hrs.	120°C cc/g/40 hrs.	200°C cc/.2g/1 hrs.
TATB		Control			0.41
	6.4×10^5	1.0×10^7			0.46
		9.0×10^7			0.57
		7.4×10^8			0.96[b]
		2.8×10^9			4.65
Tetryl		Control		2.39	Deflagrated (8 min)
	8.5×10^5	1.4×10^7	0.45	5.77	Deflagrated (3 min)
		1.2×10^8	3.08	11+(16 hrs)	Deflagrated (3 min)
		1.0×10^9	11+(10 hrs), 6.98		
TNB		Control	0.46		0.08
	9.2×10^5	1.5×10^7	0.24		0.22
		1.3×10^8			0.39
		1.0×10^9	4.10		1.45
TNT		Control	0.10	0.46	
	6.4×10^5	1.0×10^7	0.14		
		1.0×10^8	1.16		
		1.0×10^9	4.22		

NOTES: a. For a 0.52 gram sample
b. Tested for one hour
c. For a 0.51 gram sample

2. Weight Loss Measurements

The explosive powder samples were weighed in the quartz vials while the pressed pellets were weighed directly. The dimensional measurements were made within ± 0.0005 inch. The densities of the explosive pellets were determined from weight and dimensional data. The dimensional changes due to the effects of total gamma dose in the explosive pellets are shown in Table 2. The weight losses of the explosives in powder form as a function of total gamma dose are shown in Figure 2 while the weight losses of the explosives in pellet form are shown in Figure 3.

3. Differential Thermal Analysis (DTA)

The DTA studies were conducted using a duPont 900 Differential Thermal Analyzer at a heating rate of 20°C/minute while in a nitrogen atmosphere. In this thermal study the temperature differential between the material under investigation and a thermally inert reference sample was measured. The onset and peak values in the endotherms and exotherms were recorded. Comparisons were made with the same values obtained in the thermograms for the irradiated explosives. The unirradiated material is referred to as the standard or control sample and comparisons were made as a function of the total gamma dose. The results are listed in Table 3 and the DTA thermograms for each of the explosives are depicted in Figures 4 through 14. In these figures the peak values in the endotherms and exotherms are annotated.

4. Thermogravimetric Analyses (TGA)

Another thermal parameter which was measured as a function of temperature was the change in mass. The volitization of a substance can be followed by the standard non-isothermal thermogravimetric method. By this procedure decomposition which results in gaseous products is detected, and a quantitative measure of the amount and rate of decomposition at each temperature. The TGA thermograms are sufficiently reproducible to permit the determination of the temperature-stability ranges of the explosive materials. The thermogravimetric studies were performed with the duPont 950 Thermal Gravimetric Analyzer (TGA) which is an attachment to the duPont 900 DTA. In this study, normally a 20°C/min. heating rate (which was the rate used in the DTA studies) was used, and the temperature at which a 10% weight loss occurred was recorded. Also for several of the explosives other heating rates (10°C/min., 50°C/min. and 80°C/min.) were used and the temperature was noted in which the total or maximum weight loss was believed to have occurred. The results obtained as a function of total dose are listed in Table 4.

TABLE 2

DIMENSIONAL CHANGES IN EXPLOSIVE PELLETS AS FUNCTION OF TOTAL GAMMA EXPOSURE

Explosive	Total Exposure R	Weight Loss %	Diameter Change %	Length Change %	Density Change %
DATB	1.1×10^7	0.02	N.C.	N.C.	N.C.
	1.3×10^8	0.1	N.C.	+0.13	-0.4
	1.1×10^9	0.5	N.C.	+0.13	-0.5
HMX	1.1×10^7	0.13	N.C.	N.C.	N.C.
	1.3×10^8	1.0	+1.4	+1.2	-4.5
	1.1×10^9	Pellets Crumbled			
NGu	1.3×10^7	0.4	N.C.	0.03	-0.2
	1.1×10^8	Pellets Crumbled			
PETN	1.0×10^7	0.22	+0.02	+0.03	-0.4
	9.0×10^7	7.1	+0.41	N.C.	-7.6
RDX	1.0×10^7	0.33	+0.08	+0.24	-0.7
	1.0×10^8	Pellets Very Soft - Crumbled on Contact - Strong Odor			
TACOT	1.1×10^7	N.C.	N.C.	N.C.	N.C.
	1.3×10^8	0.1	N.CCC.	N.C.	-0.3
	1.1×10^9	0.1	N.C.	N.C.	-0.3
TATB	1.1×10^7	0.03	N.C.	N.C.	-0.04
	1.3×10^8	0.2	+0.03	+0.04	-0.03
	1.1×10^9	0.7	+0.2	+0.03	-0.6

TABLE 2 (Continued)

Explosive	Total Exposure R	Weight Loss %	Diameter Change %	Length Change %	Density Change %
Tetryl	1.1×10^7	0.04	N.C.	N.C.	N.C.
	1.3×10^8	0.42	+0.51	+0.44	-1.9
	1.0×10^9	8.1	+0.3	+0.8	-9.3
TNB	1.0×10^8	0.4	+2.0	+3.5	-7.0
	1.0×10^9	Pellets Were All Broken with Strond Odor Present			
TNT	1.0×10^7	0.05	+0.01	+0.02	N.C.
	1.0×10^8	0.12	+0.8	+0.09	-2.6
	1.0×10^9	3.1	+1.5	+2.1	- 7.7

NOTES: a. N.C. = Neglibible Change
b. Exposure Rate - 7.0×10^5 R/hr.
c. All mass measurements $\pm$ 0.2 mg.

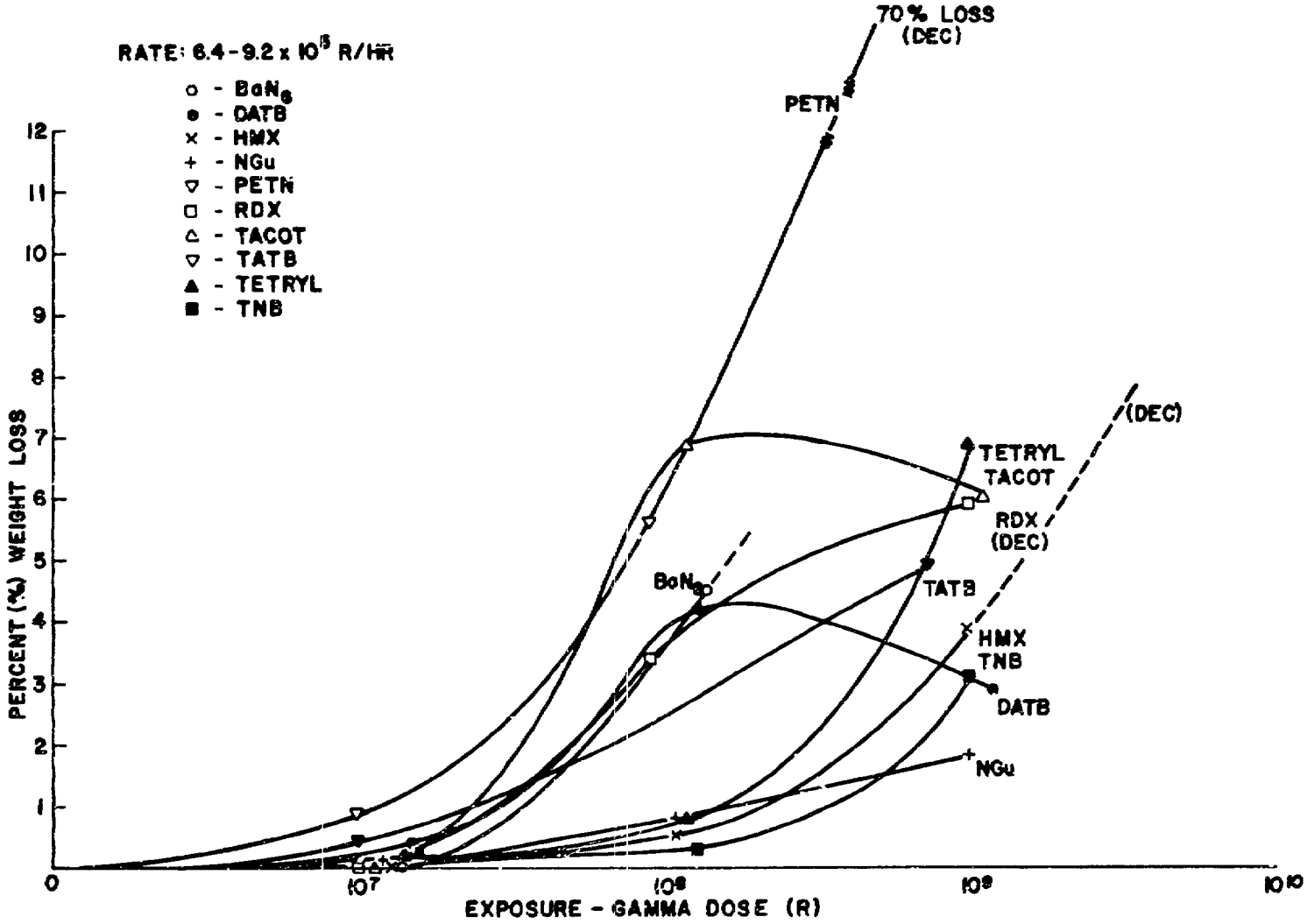

FIGURE 2 Weight Loss of Explosives Irradiated in Powder Form

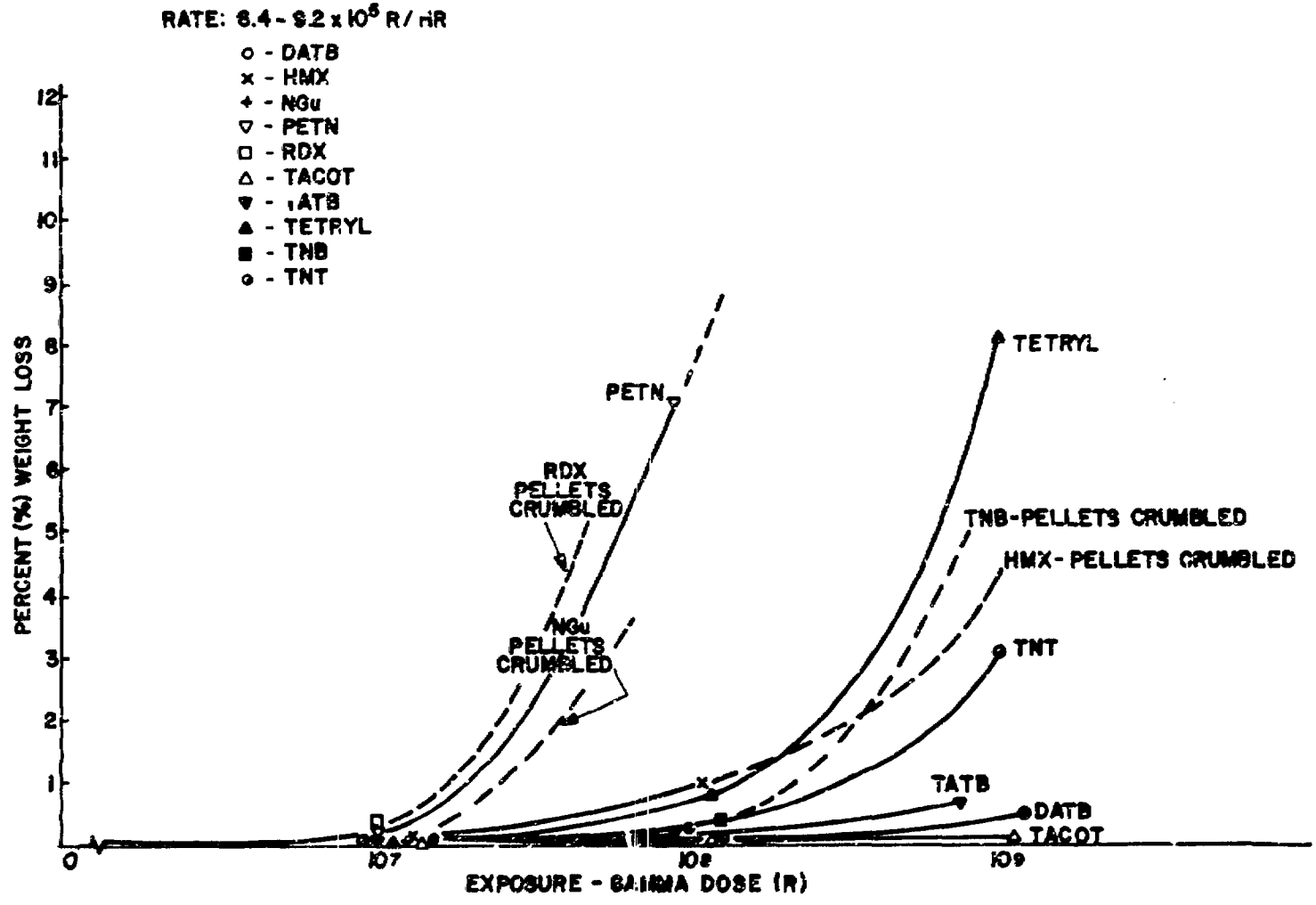

FIGURE 3 Weight Loss of Explosives Irradiated in Pellet Form

TABLE 3

DIFFERENTIAL THERMAL ANALYSIS (DTA) DATA FOR IRRADIATED EXPLOSIVES

Heating & Rate: 20°C/min.

Explosive	Total Dose R	Endotherms 1st Onset-°C	Endotherms 1st Peak-°C	Endotherms 2nd Onset-°C	Endotherms 2nd Peak-°C	Exotherms 1st Onset-°C	Exotherms 1st Peak-°C	Exotherms 2nd Onset-°C	Exotherms 2nd Peak-°C	Remarks
BaN_6	0	--	--	--	--	192	210	--	--	
	1.4×10^7	--	--	--	--	138	152	162	169	
	1.2×10^8	--	--	--	--	100	126	--	--	
	1.0×10^9	--	--	--	--	262	265	--	--	Very Small Peak
DATB	0	223	227	265	282	295	313	315	353	
	1.5×10^7	213	220	260	281	290	318	333	352	
	1.3×10^8	215	224	255	280	295	334	337	352	
	1.2×10^9	230	236	264	276	290	349			
	4.0×10^9	233	240	250	273	300	343			
HMX	0	192	199	271	272	272	286			
	1.3×10^7	173	177	274	275	275	286			
	1.1×10^8	185	190			170	179	250	293	
	1.0×10^9	180	182[a]			150	172	190	270	a. small dip
NGu	0	230	240			240	249			
	1.3×10^7	230	237			237	246			
	1.1×10^8	233	235			235	241			
	1.05×10^9	229	229			229	237			
	1.44×10^9	225	226			226	234			
PETN	0	183	143			160	216			
	1.0×10^7	127	133	136	141	170	215			
	9.0×10^7	115	138			160	215			
	1.06×10^9					130	163	187	242	

TABLE 3 (Continued)

Explosive	Total Dose Explosive	Endotherms 1st Onset-°C	Endotherms 1st Peak-°C	Endotherms 2nd Onset-°C	Endotherms 2nd Peak-°C	Exotherms 1st Onset-°C	Exotherms 1st Peak-°C	Exotherms 2nd Onset-°C	Exotherms 2nd Peak-°C	Remarks
RDX	0	180	193		197	204	250			Decomp Dip
	1.0×10^7	180	194			206	252			
	9.0×10^7	175	184	190	194	205	251			Decomp Dip
	1.06×10^9	170	190			200	258			
TACOT	0					340	376			@ 2.5°C/min
	0					365	398*			*Det.
	1.4×10^7					365	398 *			
	1.2×10^8					350	398*			
	1.1×10^9					350	385*			
	3.7×10^9					320	387*			
TATB	0					325	384			
	1.0×10^7					340	377			
	9.0×10^7					320	372			
	7.4×10^8					305	369			
	2.8×10^9					300	363			
Tetryl	0	120	128			157	220	230	268	
	1.4×10^7	120	128			173	219	235	270	
	1.2×10^8	120	127			145	220	230	270	
	1.05×10^9	93	117			145	195	199	210	
	1.44×10^9	75	109			150	164	170	203	
TNB	0	110	121	325	353					
	1.5×10^7	100	119	337	347,351					
	1.3×10^8	100	120	325	356,361					
	1.0×10^9	90	112	300	349					

TABLE 3 (Continued)

Explosive	Total Dose Explosive	Endotherms 1st Onset-°C	Endotherms 1st Peak-°C	Endotherms 2nd Onset-°C	Endotherms 2nd Peak-°C	Exotherms 1st Onset-°C	Exotherms 1st Peak-°C	Exotherms 2nd Onset-°C	Exotherms 2nd Peak-°C	Remarks
TNT	0	77	81			290	324			
	1.0×10^7	77	81			280	321			
	1.0×10^8	70	77,79			260	315			
	1.0×10^9	20	71			245	290			

NOTE: Underlined temperature denotes major endotherm or exotherm.

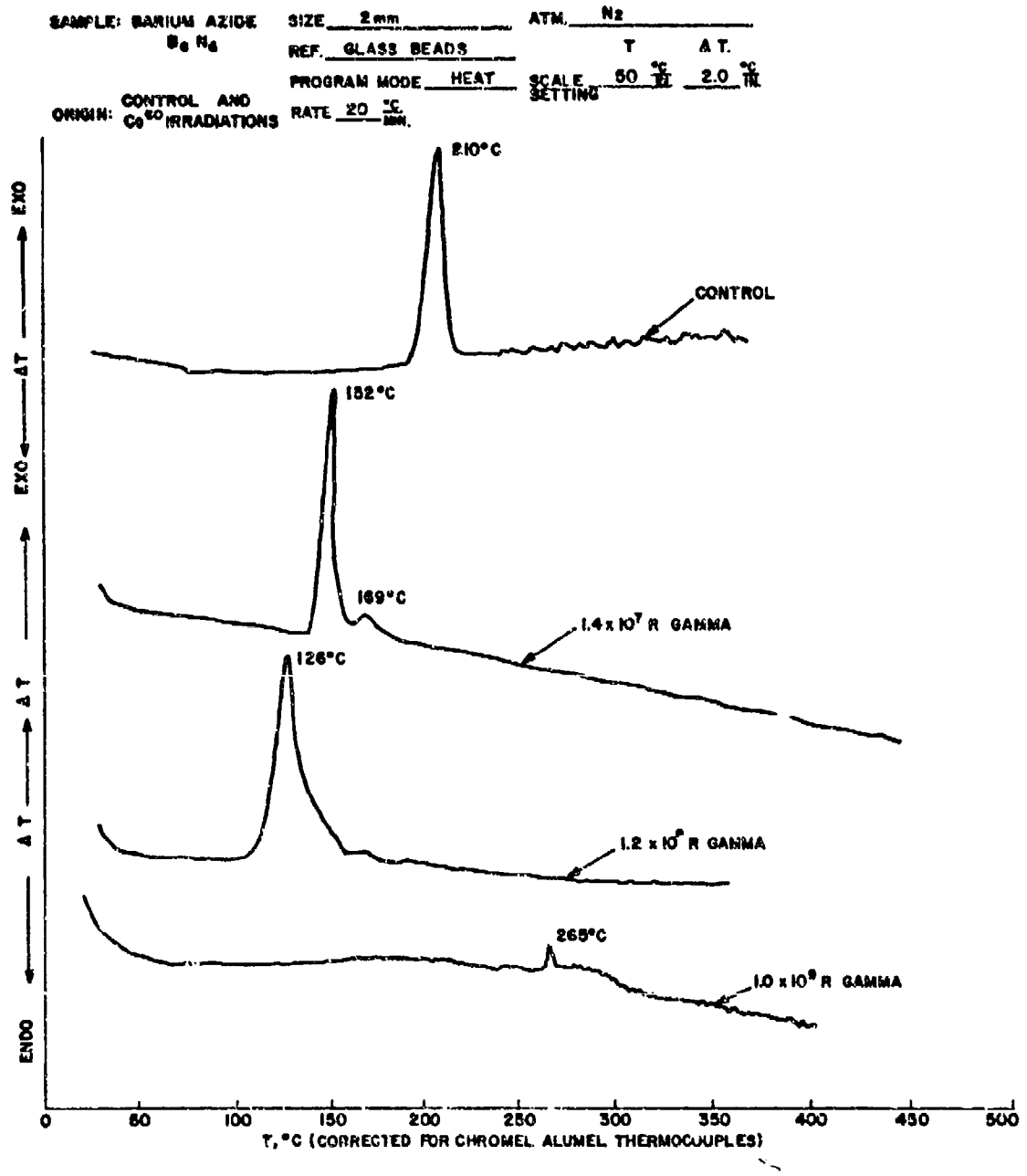

FIGURE 4 DTA Thermograms for BaN_6 as a Function of Gamma Dose

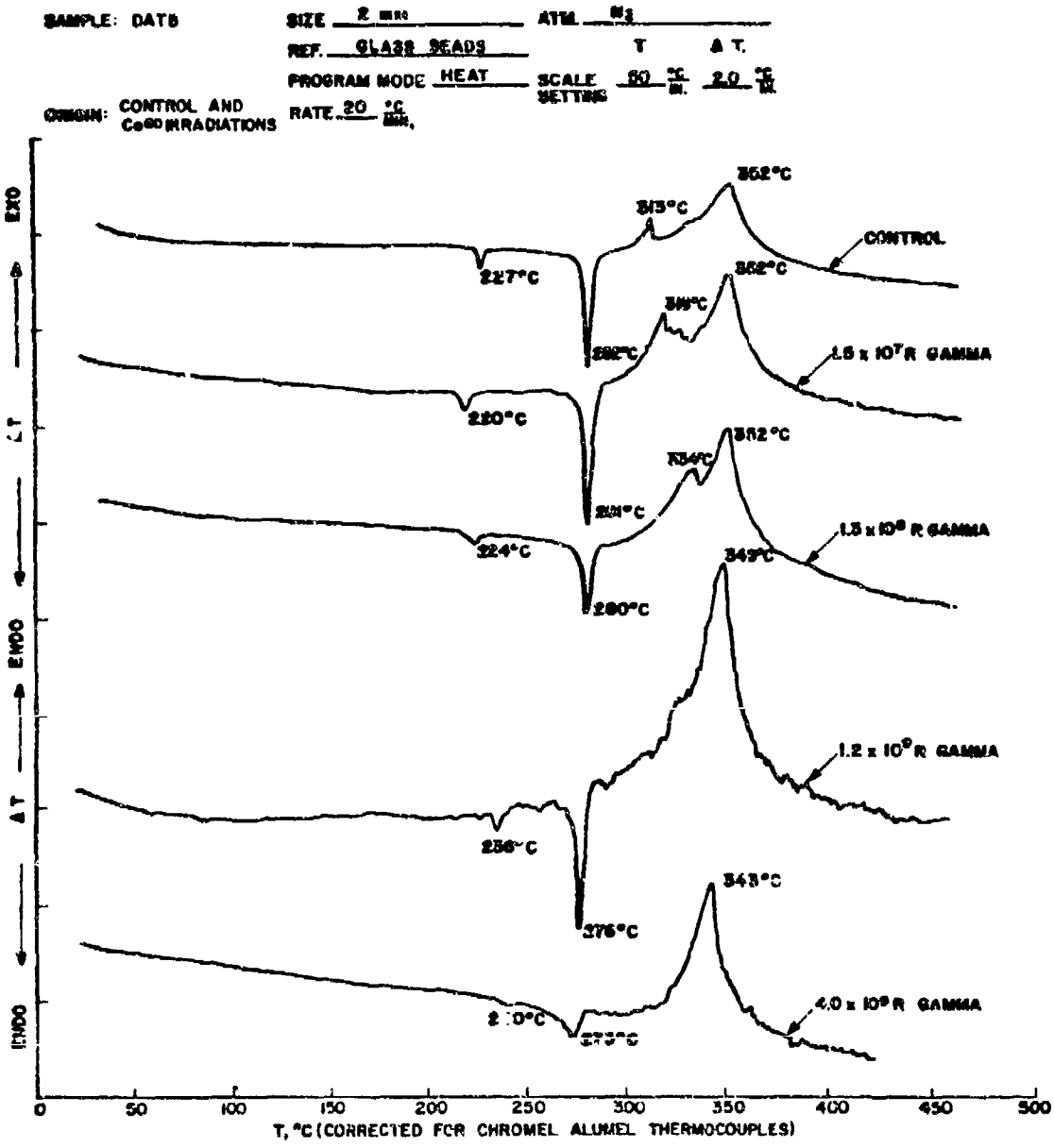

FIGURE 5 DTA Thermograms for DATB as a Function of Gamma Dose

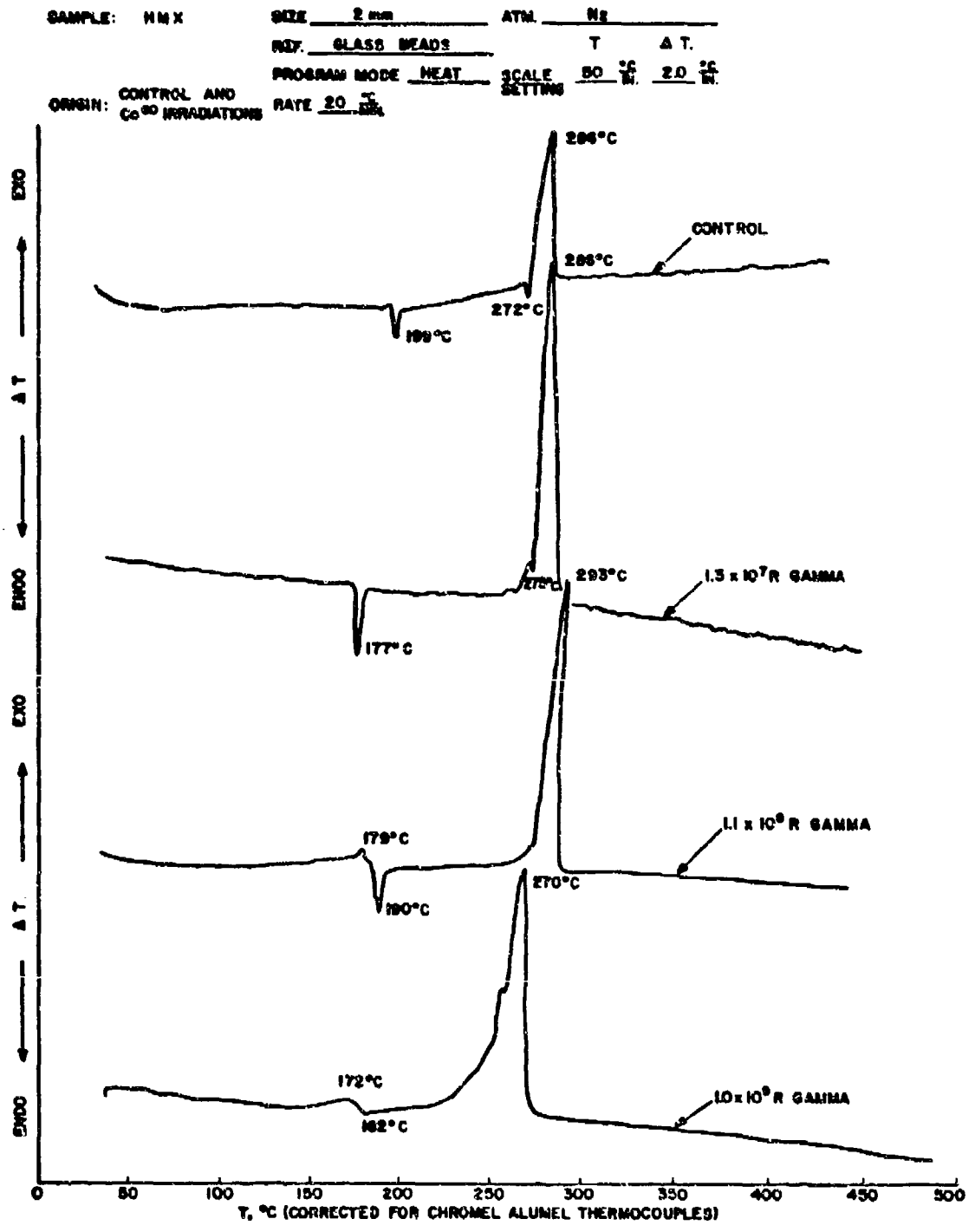

FIGURE 6 DTA Thermograms of HMX as a Function of Gamma Dose

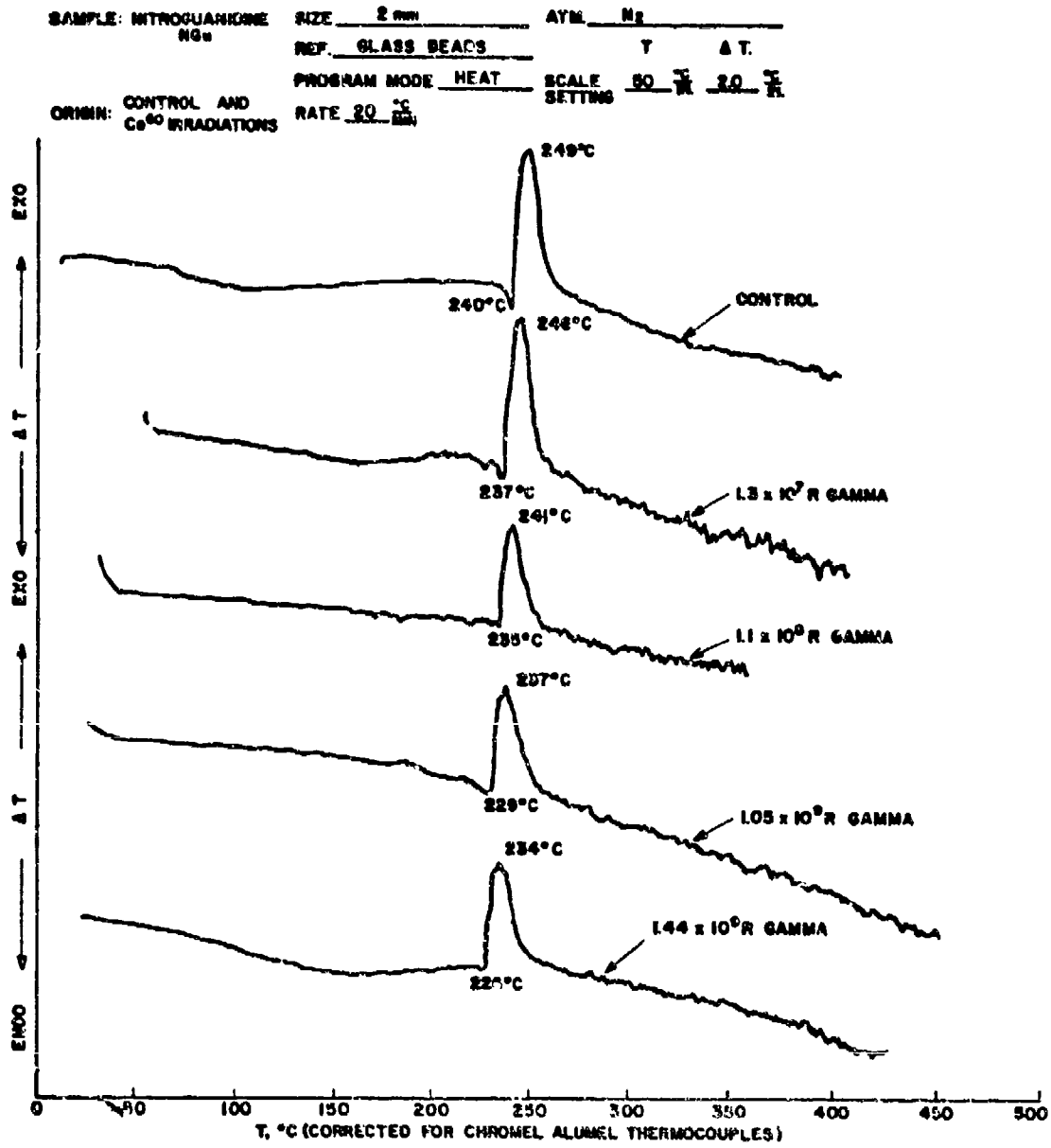

FIGURE 7 DTA Thermograms of NGu as a Function of Gamma Dose

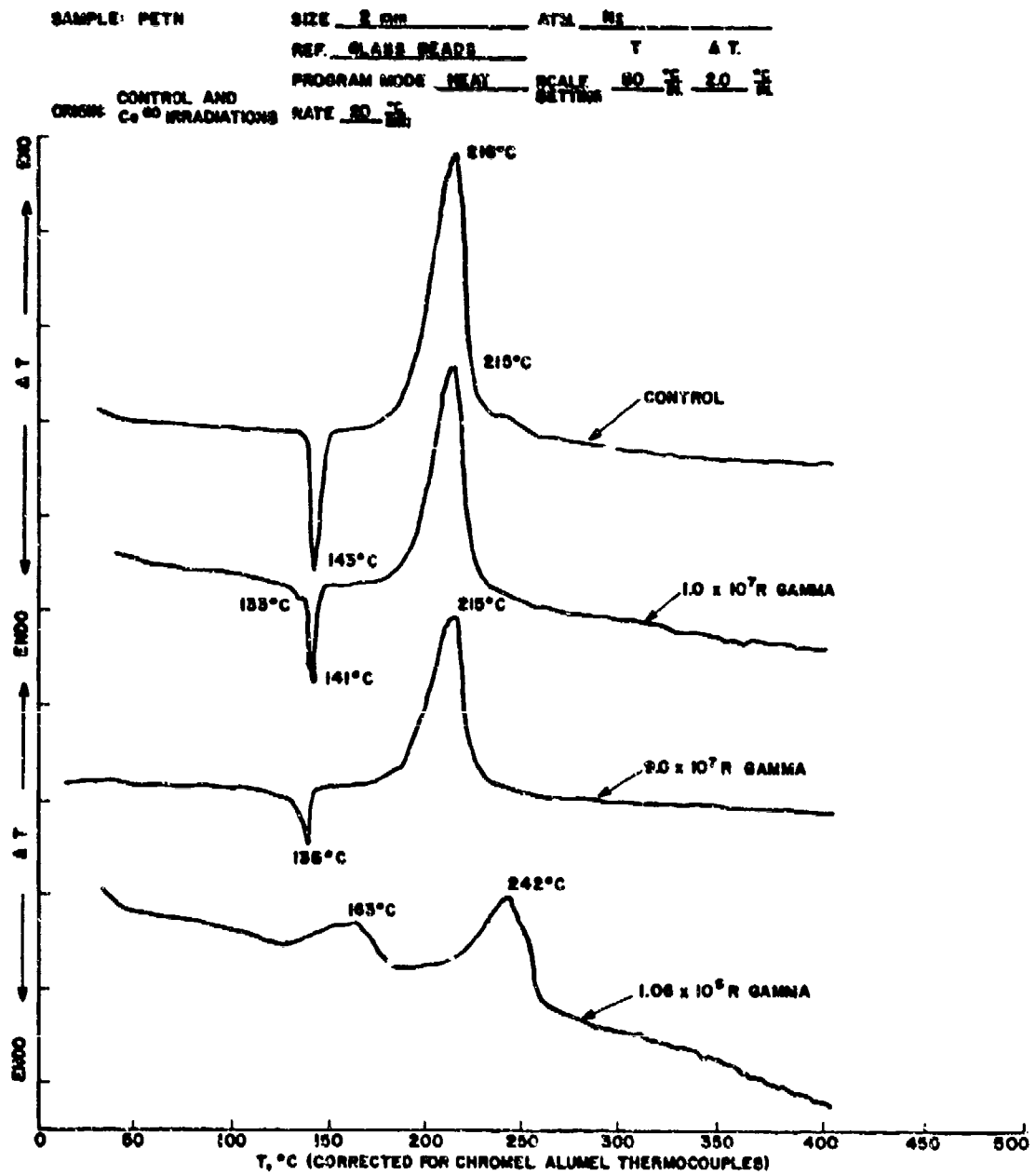

FIGURE 8 DTA Thermograms of PETN as a Function of Gamma Dose

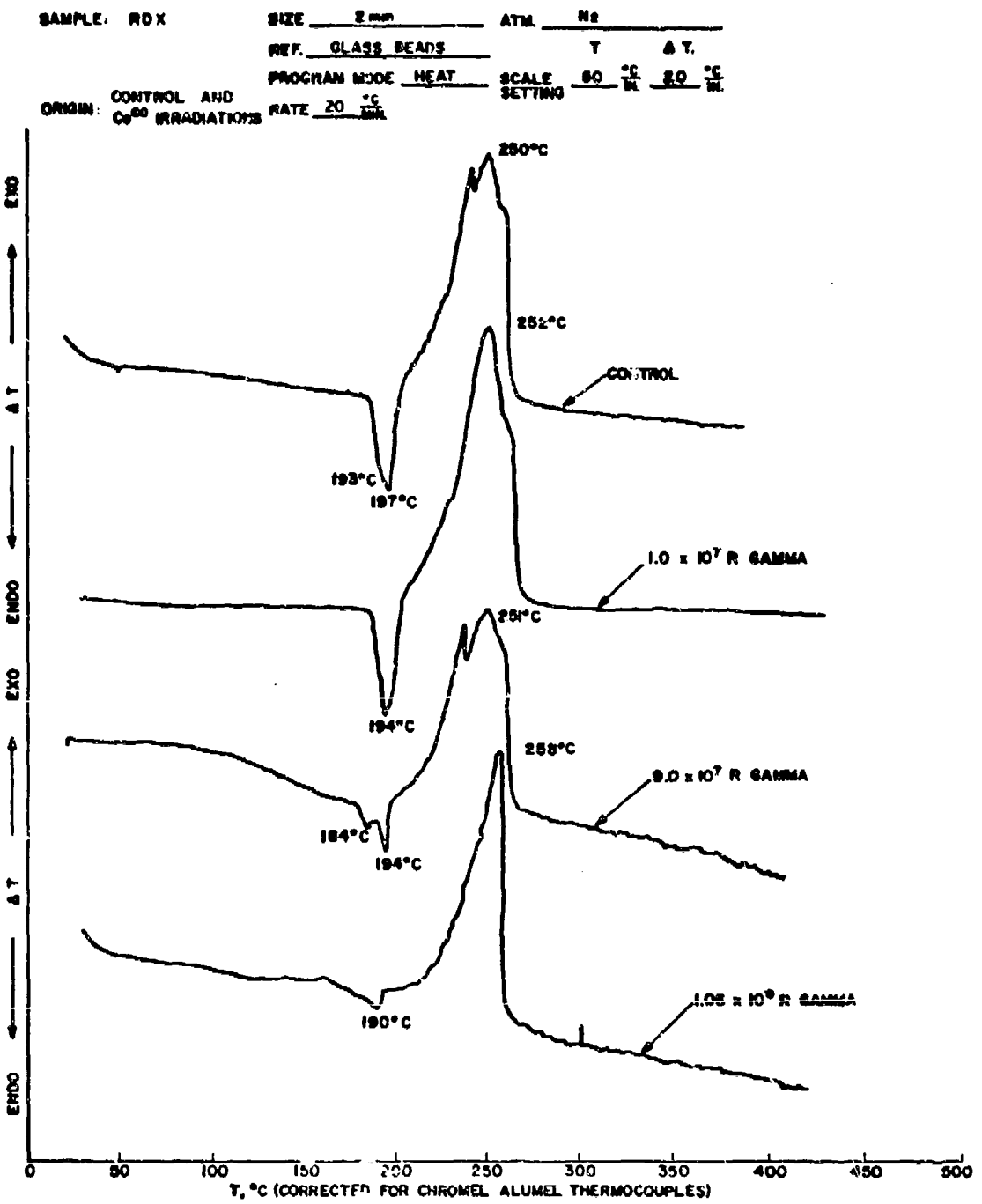

FIGURE 9 DTA Thermograms of RDX as a Function of Gamma Dose

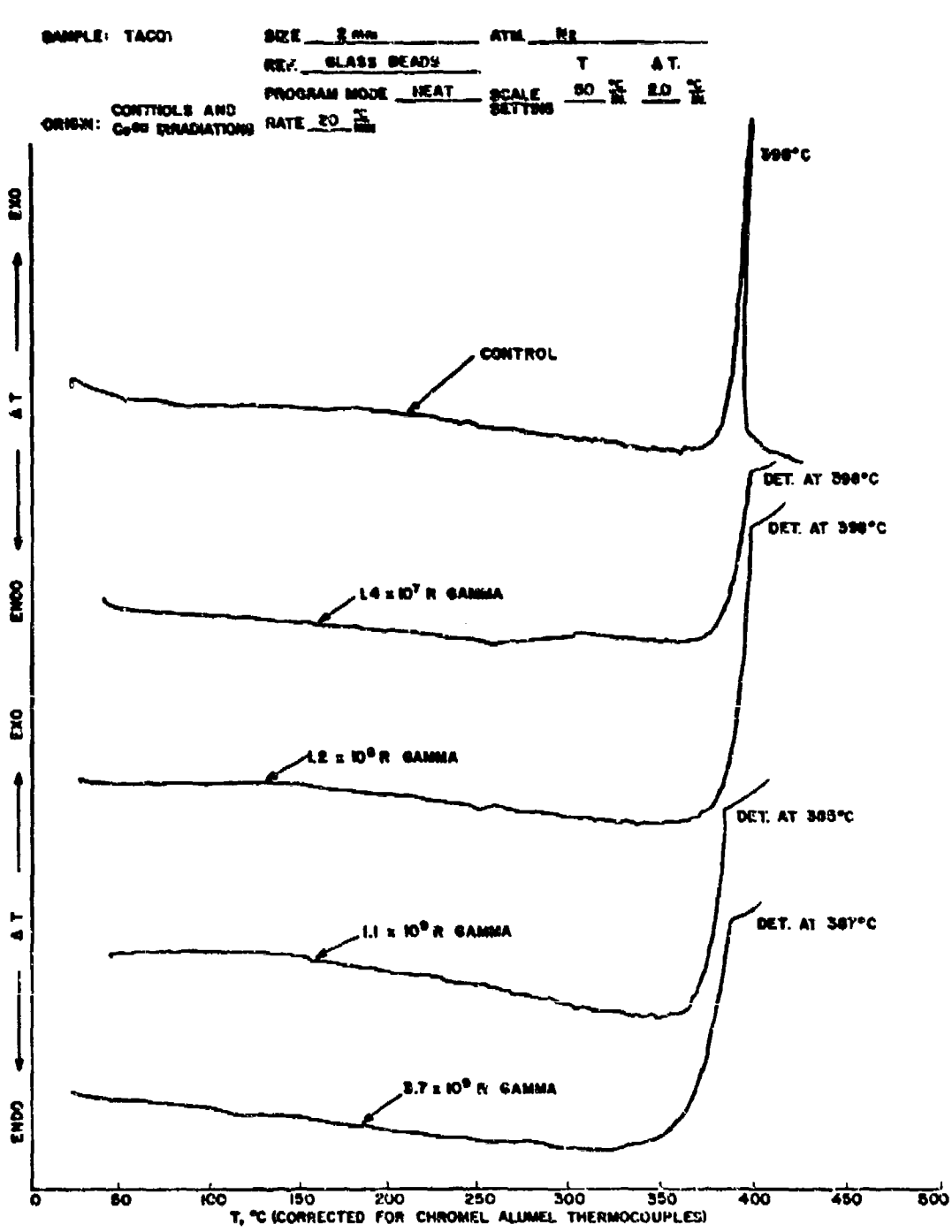

FIGURE 10 DTA Thermograms of TACOT as a Function of Gamma Dose

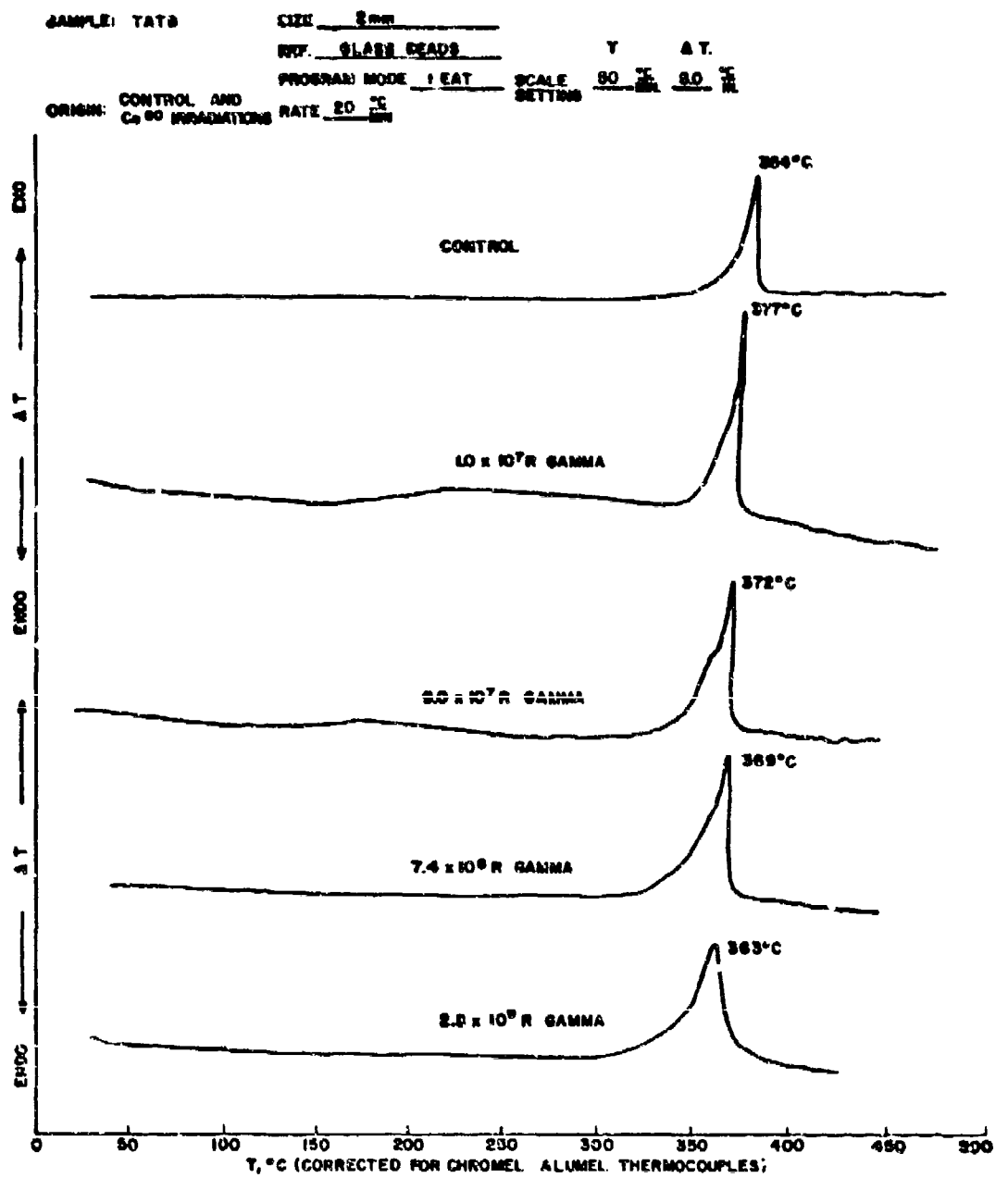

FIGURE 11 DTA Thermograms of TATB as a Function of Gamma Dose

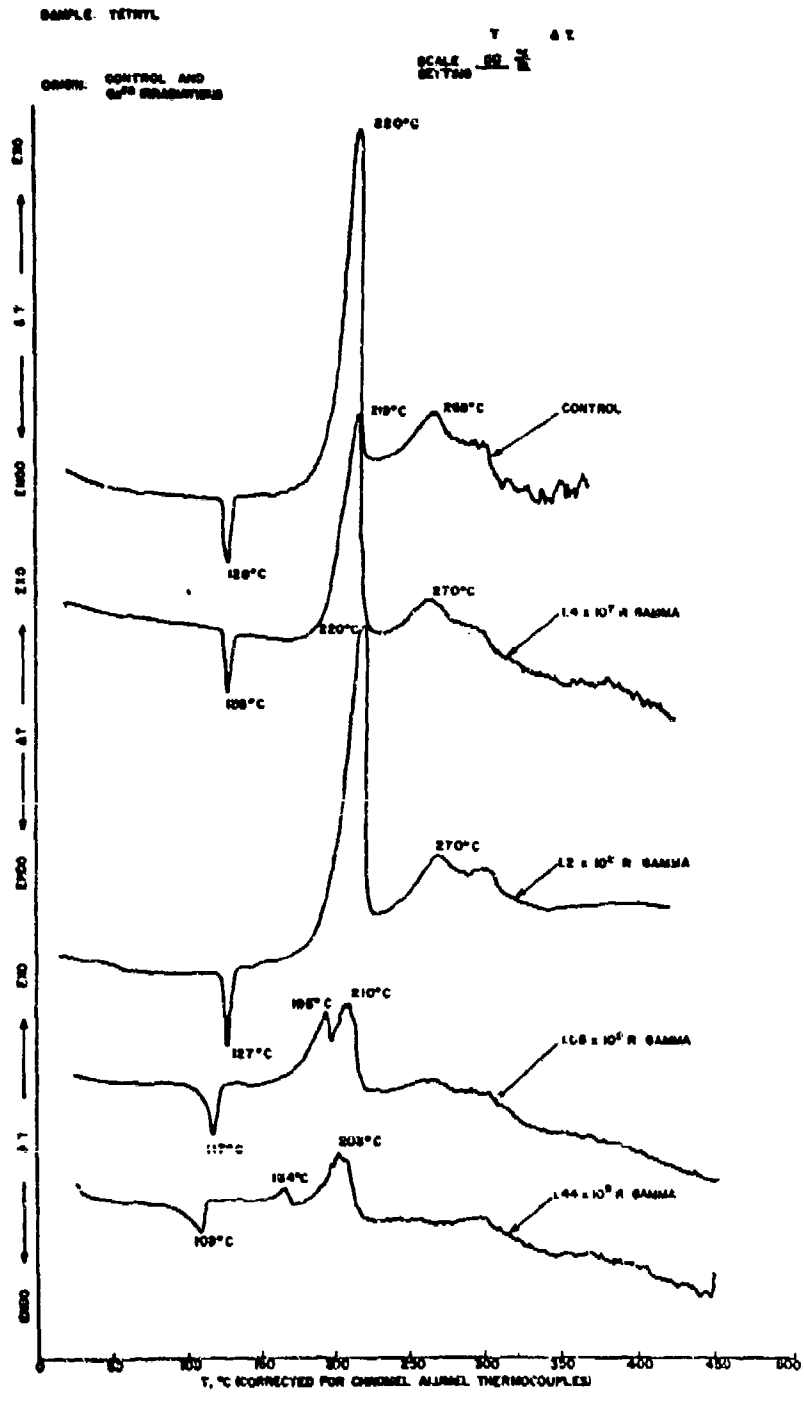

FIGURE 12 DTA Thermograms of Tetryl as a Function of Gamma Dose

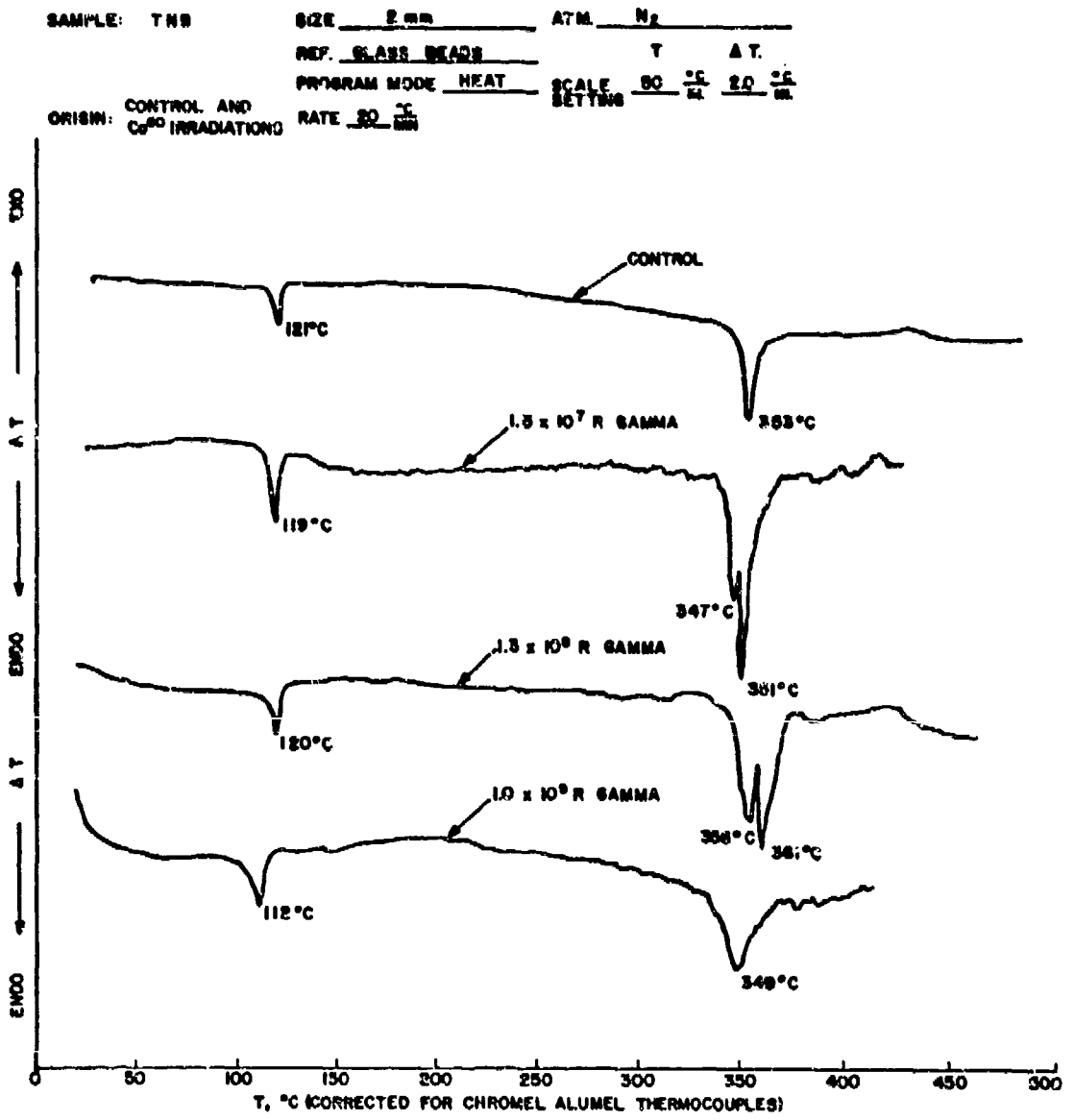

FIGURE 13 DTA Thermograms of TNB as a Function of Gamma Dose

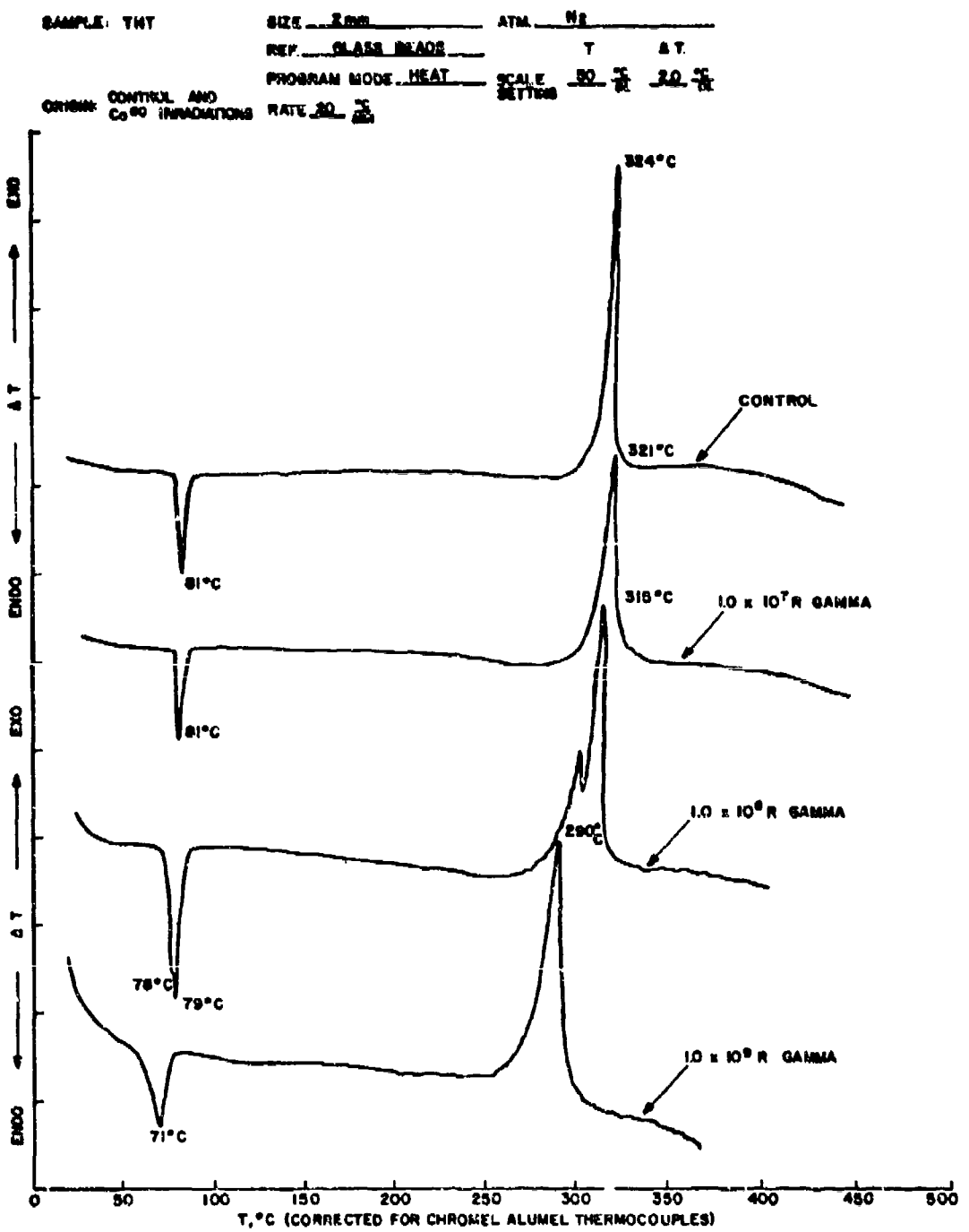

FIGURE 14 DTA Thermograms of TNT as a Function of Gamma Dose

TABLE 4

THERMOGRAVIMETRIC ANALYSIS (TGA) DATA FOR IRRADIATED EXPLOSIVES

Explosive	Total Dose R	Heating Rate	Weight mg	Start of Decomposition-°C	10% Weight Loss Temp-°C	Total Weight Loss-%	Remarks
BaN_6	0	20°C/min	4.4	190	--	>1% @ 193°C	Deflagrated @ 193°C
	1.4×10^7	20°C/min	7.5	143	--	>1% @ 145°C	Deflagrated @ 125°C
	1.2×10^8	20°C/min	8.7	100	--	>3% @ 125°C	Deflagrated @ 125°C
	1.0×10^9	20°C/min	3.7	250	--	9.5% @ 450°C	--
DATB	0	20°C/min	7.9	215	275	96% @ 345°C	--
	1.5×10^7	20°C/min	8.6	215	275	96% @ 335°C	--
	1.3×10^8	20°C/min	7.9	215	275	96% @ 350°C	--
	1.2×10^9	20°C/min	8.1	215	283	92% @ 350°C	--
	4.0×10^9	20°C/min	7.65	180	272	82% @ 340°C	--
	0	10°C/min	9.8	200	254	97% @ 330°C	--
	1.3×10^8	10°C/min	9.9	195	252	97% @ 310°C	--
	1.2×10^9	10°C/min	9.4	195	268	93% @ 330°C	--
	0	50°C/min	8.4	215	281	93% @ 355°C	--
	1.3×10^8	50°C/min	8.8	205	282	97% @ 360°C	--
	1.2×10^9	50°C/min	8.2	255	300	--	Deflagrated @ 358°C
	0	80°C/min	10.2	230	326	97% @ 410°C	
	1.3×10^8	80°C/min	8.1	210	290	97% @ 355°C	
	1.2×10^9	80°C/min	9.3	220	315	92% @ 395°C	Partial Defl @ 373°C
HMX	0	20°C/min	8.4	250	282	10% @ 282°C	Detonated @ 282°C
	1.3×10^7	20°C/min	10.9	180	266	15% @ 268°C	Detonated @ 268°C
	1.1×10^8	20°C/min	8.2	55	250	21% @ 274°C	Detonated @ 274°C
	1.0×10^9	20°C/min	8.2	105	185	24% @ 252°C	Detonated @ 252°C

TABLE 4 (Continued)

Explosive	Total Dose R	Heating Rate	Weight mg	Start of Decomposition-°C	10% Weight Loss Temp-°C	Total Weight Loss-%	Remarks
HMX	0	50°C/min	10.3	275	--	23% @ 297°C	Detonated @ 297°C
	0	80°C/min	9.5	280	--	6% @ 300°C	Detonated @ 300°C
NGu	0	20°C/min	7.7	205	248	14% @ 249°C	Deflagrated @ 249°C
	1.3×10^7	20°C/min	8.45	203	245	17% @ 249°C	Deflagrated @ 249°C
	1.1×10^8	20°C/min	8.0	185	231	22% @ 244°C	Deflagrated @ 244°C
PETN	0	20°C/min	8.3	160	187	96% @ 220°C	--
	1.0×10^7	20°C/min	8.4	135	178	97% @ 230°C	--
	9.0×10^7	20°C/min	8.15	70	177	96% @ 220°C	--
	0	50°C/min	8.45	173	200	46% @ 219°C	Deflagrated @ 219°C
	1.0×10^7	50°C/min	8.5	130	197	30% @ 212°C	Deflagrated @ 212°C
	9.0×10^7	50°C/min	8.5	70	184	50% @ 214°C	Deflagrated @ 214°C
RDX	0	20°C/min	8.9	190	230	14% @ 240°C	Deflagrated @ 240°C
	1.0×10^7	20°C/min	8.4	160	224	23% @ 240°C	Deflagrated @ 240°C
	9.0×10^7	20°C/min	8.6	38	63	40% @ 240°C	Deflagrated @ 240°C
TACOT	0	20°C/min	8.4	350	--	7% @ 406°C	Detonated @ 406°C
	1.4×10^7	20°C/min	7.2	340	--	7% @ 387°C	Detonated @ 387°C
	1.2×10^8	20°C/min	9.7	320	--	8% @ 372°C	Detonated @ 372°C
	1.1×10^9	20°C/min	9.9	320	--	9% @ 387°C	Detonated @ 387°C
	3.7×10^9	20°C/min	8.5	240	354	18% @ 370°C	Detonated @ 370°C
	7.0×10^9	20°C/min	10.75	180	330	17% @ 355°C	Detonated @ 355°C
TATB	0	20°C/min	9.6	285	353	83% @ 420°C	--
	1.0×10^7	20°C/min	6.9	280	341	80% @ 400°C	--
	9.0×10^8	20°C/min	8.8	250	327	80% @ 385°C	--
	7.4×10^9	20°C/min	9.6	250	329	77% @ 405°C	--
	2.8×10^9	20°C/min	8.6	125	303	52% @ 345°C	Detonated @ 345°C
	7.0×10^9	20°C/min	8.3	125	299	52% @ 342°C	Detonated @ 342°C

TABLE 4 (Continued)

Explosive	Total Dose R	Heating Rate	Weight mg	Start of Decomposition-°C	10% Weight Loss Temp-°C	Total Weight Loss-%	Remarks
TATB	1.0×10^7	10°C/min	9.25	260	321	81% @ 375°C	--
	9.0×10^7	10°C/min	8.3	230	294	77% @ 340°C	--
	0	50°C/min	9.55	275	363	82% @ 440°C	--
	1.0×10^7	50°C/min	8.0	250	351	81% @ 420°C	2 Step Decomp.
	9.0×10^9	50°C/min	7.9	235	332	82% @ 390°C	2 Step Decomp.
	2.8×10^9	50°C/min	9.8	225	--	9% @ 342°C	Detonated @ 342°C
	0	80°C/min	8.0	310	375	85% @ 420°C	--
	1.0×10^7	80°C/min	7.9	290	363	80% @ 435°C	2 Step Decomp.
	9.0×10^9	80°C/min	7.6	265	330	81% @ 395°C	2 Step Decomp.
	2.8×10^9	80°C/min	8.4	260	350	10% @ 350°C	Detonated @ 350°C
Tetryl	0	20°C/min	9.8	180	--	7% @ 215°C	Detonated @ 214°C
	1.4×10^8	20°C/min	9.7	180	--	8% @ 216°C	Detonated @ 216°C
	1.2×10^8	20°C/min	10.0	140	--	7% @ 212°C	Detonated @ 212°C
TNB	0	20°C/min	8.2	155	218	97% @ 285°C	--
	1.5×10^8	20°C/min	8.8	155	208	95% @ 265°C	--
	1.3×10^9	20°C/min	8.5	150	209	97% @ 275°C	--
	1.0×10^9	20°C/min	7.4	125	180	97% @ 245°C	--
	0	10°C/min	8.3	130	188	94% @ 245°C	--
	1.5×10^8	10°C/min	8.2	135	192	97% @ 247°C	--
	1.3×10^8	10°C/min	8.75	130	189	99% @ 250°C	--
	0	50°C/min	8.0	175	248	95% @ 325°C	--
	1.5×10^8	50°C/min	8.2	160	236	98% @ 305°C	--
	1.3×10^8	50°C/min	8.1	160	232	96% @ 300°C	--

TABLE 4 (Continued)

Explosive	Total Dose R	Heating Rate	Weight mg	Start of Decomposition-°C	10% Weight Loss Temp-°C	Total Weight Loss-%	Remarks
TNB	0	80°C/min	9.2	195	267	96% @ 355°C	--
	1.5×10^7	80°C/min	8.7	175	251	97% @ 330°C	--
	1.3×10^8	80°C/min	7.9	170	242	95% @ 320°C	--
TNT	0	20°C/min	7.4	135	190	99% @ 250°C	--
	1.0×10^7	20°C/min	7.4	135	190	96% @ 255°C	--
	1.0×10^8	20°C/min	8.7	115	185	95% @ 255°C	--
	1.0×10^9	20°C/min	7.1	110	173	86% @ 235°C	--
	0	50°C/min	8.4	150	212	97% @ 275°C	--
	0	80°C/min	9.6	160	224	98% @ 300°C	--

b. Purity

1. Melting Points and Color Change

The melting points were obtained to determine the changes caused by ionizing radiation in the purity of each explosive material. Also from a visual point the color changes were noted for each dosage. The results are given in Table 5. As can be expected the principal effect on practically all the explosives was to lower their melting points. This can also be compared to the endotherms in the DTA thermograms.

2. Infrared Spectra (IR)

Infrared absorption can be used for the identification of a pure compound and for the detection of significant changes in the molecular structure of a compound which has been subjected to a particular environment. Usually these changes are indicated by the disappearance or appearance of bands, or a combination of both. The detection of these changes usually depends on the nature of the reaction product or impurity and its concentration, which usually must be greater than one percent.

The infrared (IR) spectra for the explosives were obtained by the KBr (potassium bromide) pellet technique before and after irradiation. The spectrum of the irradiated sample compared to that of the control. The IR spectra of all the explosives except BaN_6 did not indicate any significant changes when compared to the control IR spectra. The changes in BaN_6 are shown in Figure 15 which will be discussed later.

c. Sensitivity

To determine the effects of gamma radiation on the sensitivity characteristics of the explosives studied, the tests selected were the impact sensitivity test (mechanical stimulus) and the explosion temperature test (thermal sensitivity).

1. Impact Sensitivity

To measure the sensitivity of an explosive sample to mechanical impact, the Picatinny Arsenal impact machine was used. With a 2 kg dropweight the height of fall in inches which produces explosions in 50% of the samples tested is the reported impact sensitivity index. The procedure used to determine the 50% point was the Bruceton up-and-down method.

TABLE 5

EFFECT OF GAMMA RADIATION ON THE ME NG POINT AND COLOR OF EXPLOSIVES

Explosive	Total Dose R	Melting Point °C	Color	
BaN_6	0	201.5	White	
	1.4×10^7	205.5	White	
	1.2×10^8	--	White	Exploded @ 260
	1.0×10^9	--	White	No Reaction @ 290
DATB	0	283.5	Yellow	
	1.5×10^7	283.5	Yellow Green	
	1.3×10^8	282.5	Green	
	1.2×10^9	281.5	Dark Brown	
	4.0×10^9		Purplish Brown	
HMX	0	273.5	White	
	1.3×10^7	271.0	White	
	1.1×10^8	271.0	White	
	1.0×10^9	255 Dec.	White	
NGu	0	239	White	
	1.3×10^7	237	Off White	
	1.1×10^8	232	Yellowish White	
	1.0×10^9		White	
PETN	0	141.5	White	
	1.0×10^7	141.5	White	
	9.0×10^7	136	White	
	1.06×10^9		White Paste	
RDX	0	197.5	White	
	1.0×10^7	198	White	
	9.0×10^7	203	White	
	1.06×10^9	191 Dec.	White Paste	
TACOT	0	390 Dec.	Red Orange	
	1.4×10^7	390 Dec.	Red Orange	
	1.2×10^8	388 Dec.	Brownish Orange	
	1.1×10^9	378 Dec.	Reddish Dark Brown	
	3.7×10^9		Maroon Dark Brown	

TABLE 5 (Continued)

Explosive	Total Dose R	Melting Point °C	Color
TATB	0	400 Dec.	Yellow
	1.0×10^7	400 Dec.	Yellow Green
	9.0×10^7	400 Dec.	Green
	7.4×10^8	400 Dec.	Dark Green
	2.8×10^9	400 Dec.	Blackish Green
Tetryl	0	129	Yellow
	1.4×10^7	129	Dark Yellow
	1.2×10^8	128	Brownish Yellow
	1.0×10^9		Brownish Yellow
TNB	0	120	Pale Yellow
	1.5×10^7	120	Yellow
	1.3×10^8	120	Yellow
	1.0×10^9	113	Brown
TNT	0	81.5	Light Yellow
	1.0×10^7	80.5	Yellow
	1.0×10^8	78.5	Dark Yellow
	1.0×10^9		Brownish Yellow

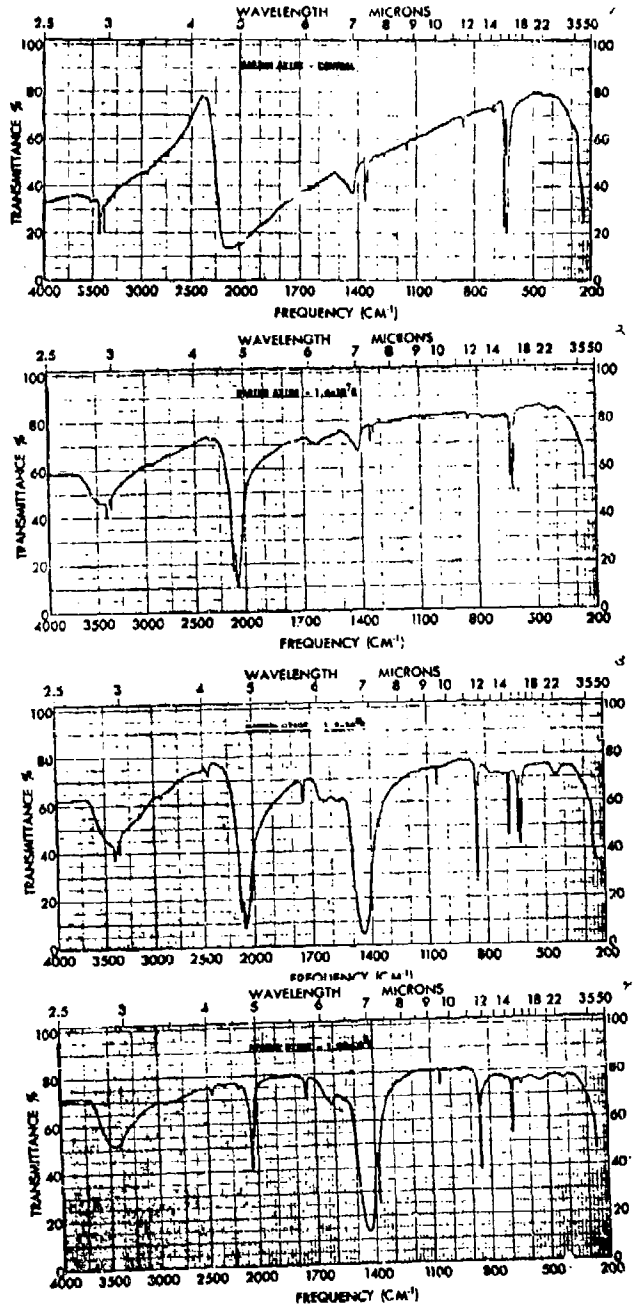

FIGURE 15 Infrared Spectra for BaN_6 Before and After Gamma Radiation

The Bruceton 50% fire values for the control and irradiated explosives are listed in Table 6. The gamma radiation did not affect the impact sensitivity of all the explosives the same way. Some explosives showed an increase, some a decrease and others essentially no change in sensitivity. However, in every case at the uppermost dose levels the "go" values did not sound as powerful as those for the control samples.

2. Explosion Temperature

The explosion temperature test is used as a means of determining the thermal sensitivity of an explosive material. By this method the time to explosion for a given temperature is determined for an explosive. The relationship for explosive materials between the time to explosion and the temperature T is expressed by the expression:

$$t = Ae^{E_a/RT} \tag{1}$$

where E_a is the activation energy in kcal/mole, A is a constant dependent on the geometry of the experiment and the composition of the explosive, T is the explosion temperature in °K, and R is the universal gas constant. In logarithmic form this equation is

$$\ln t = \ln A + E_a/RT \tag{2}$$

In the plot of ln t vs T^{-1}, the slope of the straight line obtained is equal to E_a/RT permitting the determination of E_a which, in reality, is only an apparent activation energy since the entire explosive is not subjected simultaneously to isothermal heating. The confined or closed method of obtaining the explosion temperature curves was first proposed by Henkin and McGill[4] and modified by Zinn and Rogers[5] and others[6,7]. Figures 16 through 26 display the explosion temperature curves for all of the explosives before and after irradiation. The apparent activation energies were obtained from the slope of each curve which was determined by the least square method. These are listed with the 5-second explosion temperature for each explosive in Table 7. The effect of total gamma dose on the 5-second explosion temperature for each explosive is shown in Figure 27.

d. Detonation Velocity

The rates of detonation were measured by the pin machine technique. The method utilizes ionization-operated pin switches located along the rate stick (explosive charge) at known distances.

TABLE 6

IMPACT SENSITIVITY DATA FOR IRRADIATED EXPLOSIVES

- 50% FIRE HEIGHT IN INCHES BY BRUCETON METHOD -

Explosive	Total Co^{60} Gamma Dose-R	$\bar{X}$-Mean-Inches	σ-Std. Dev.-Inches
BaN_6	0	11.22	1.30
	1.4×10^7	7.03	5.18
	1.2×10^8	11.42	1.67
	1.0×10^9	36+ (a)	--
DATB	0	20.64(b)	6.20
	1.5×10^7	19.00	1.26
	1.3×10^8	17.80	1.99
	1.2×10^9	13.50	1.51
HMX	0	14.04	1.04
	1.3×10^7	11.04	1.44
	1.1×10^8	8.96	2.57
	1.0×10^9	9.96	2.40
NGu	0	27.78	2.22
	1.3×10^7	20.70	2.21
	1.1×10^8	24.83	1.49
	1.0×10^9	36+ (a)	--
PETN	0	9.23	4.47
	1.0×10^7	7.69	3.28
	9.0×10^7	7.56	7.45
	1.0×10^9	(c)	--
RDX	0	14.75	3.86
	1.0×10^7	14.30	0.63
	9.0×10^7	11.50	0.76
	1.0×10^9	(c)	--
TACOT	0	12.0	1.86
	1.4×10^7	12.5	1.34
	1.2×10^8	12.32	1.25
	1.1×10^9	11.83	2.28
TATB	0	22.16	3.19
	1.0×10^7	17.6	1.28
	9.0×10^7	18.39	0.93
	7.4×10^8	17.1	3.12

TABLE 6 (Continued)

Explosive	Gamma Dose-R	$\bar{X}$-Mean-Inches	σ-STD. Dev.-Inches
Tetryl	0	17.3	0.96
	1.4×10^7	16.2	0.81
	1.2×10^8	19.5	0.86
	1.0×10^9	18.25	3.28
TNB	0	23.26	4.58
	1.5×10^7	18.5	2.96
	1.3×10^8	20.5	1.89
	1.0×10^9	32.5	4.15
TNT	0	25.5	7.48
	1.0×10^7	26.5	8.41
	1.0×10^8	--	--
	1.0×10^9	30.11	5.55

NOTES: 2 kg drop weight with Picatinny Arsenal impact apparatus - room temp. 70°F - rel. um. 53%

(a) No detonation in 25 trials.
(b) All DATB data based on burned, no explosion.
(c) Explosive became gummy during irradiation and stuck in vial.

TABLE 7

EFFECT OF GAMMA RADIATION ON EXPLOSION TEMPERATURE AND APPARENT ACTIVATION ENERGY OF EXPLOSIVES

Explosive	Total Dose R	5 Second Explosion Temp. °C	Apparent Activation Energy Kcal/Mole
BaN_6	0	312	26.32
	1.2×10^8	249	18.85
DATB	0	396	14.44
	1.5×10^7	384	17.83
	1.3×10^8	373	15.95
	1.2×10^9	365	17.74
HMX	0	300	14.45
	1.3×10^7	290	16.36
	1.1×10^8	286	23.50
	1.0×10^9	201	6.10
NGu	0	288	17.91
	1.3×10^7	282	14.72
	1.1×10^8	285	15.04
PETN	0	228	18.12
	9.0×10^7	222	14.16
RDX	0	261	14.15
	9.0×10^7	249	14.61
TACOT	0	415	31.14
	1.4×10^7	411	26.16
	1.2×10^8	407	26.58
	1.1×10^9	404	27.50
TATB	0	403	19.30
	1.0×10^7	394	18.91
	9.0×10^7	370	16.18
	7.4×10^8	345	29.28
Tetryl	0	243	14.18
	1.2×10^8	236	13.52

TABLE 7 (Continued)

Explosive	Total Dose R	5 Second Explosion Temp. °C	Apparent Activation Energy Kcal/Mole
TNB	0	452	24.86
	1.5×10^7	434	42.28
	1.3×10^8	458	19.47
TNT	0	396	21.70
	1.0×10^7	389	15.05
	1.0×10^8	394	18.37
	1.0×10^9	345	19.23

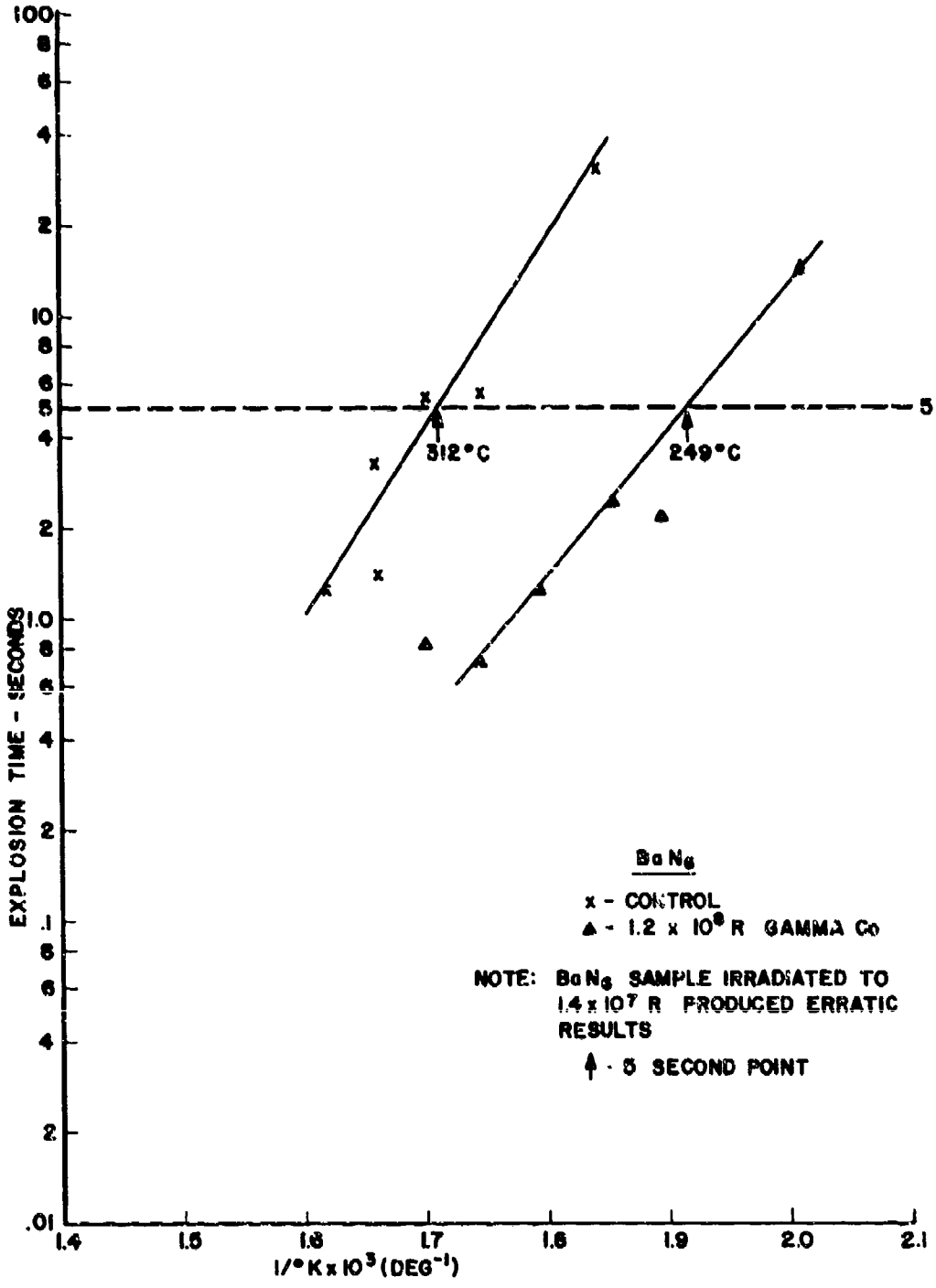

FIGURE 16 Explosion Temperature Curves for BaN_6 Before and After Gamma Irradiation

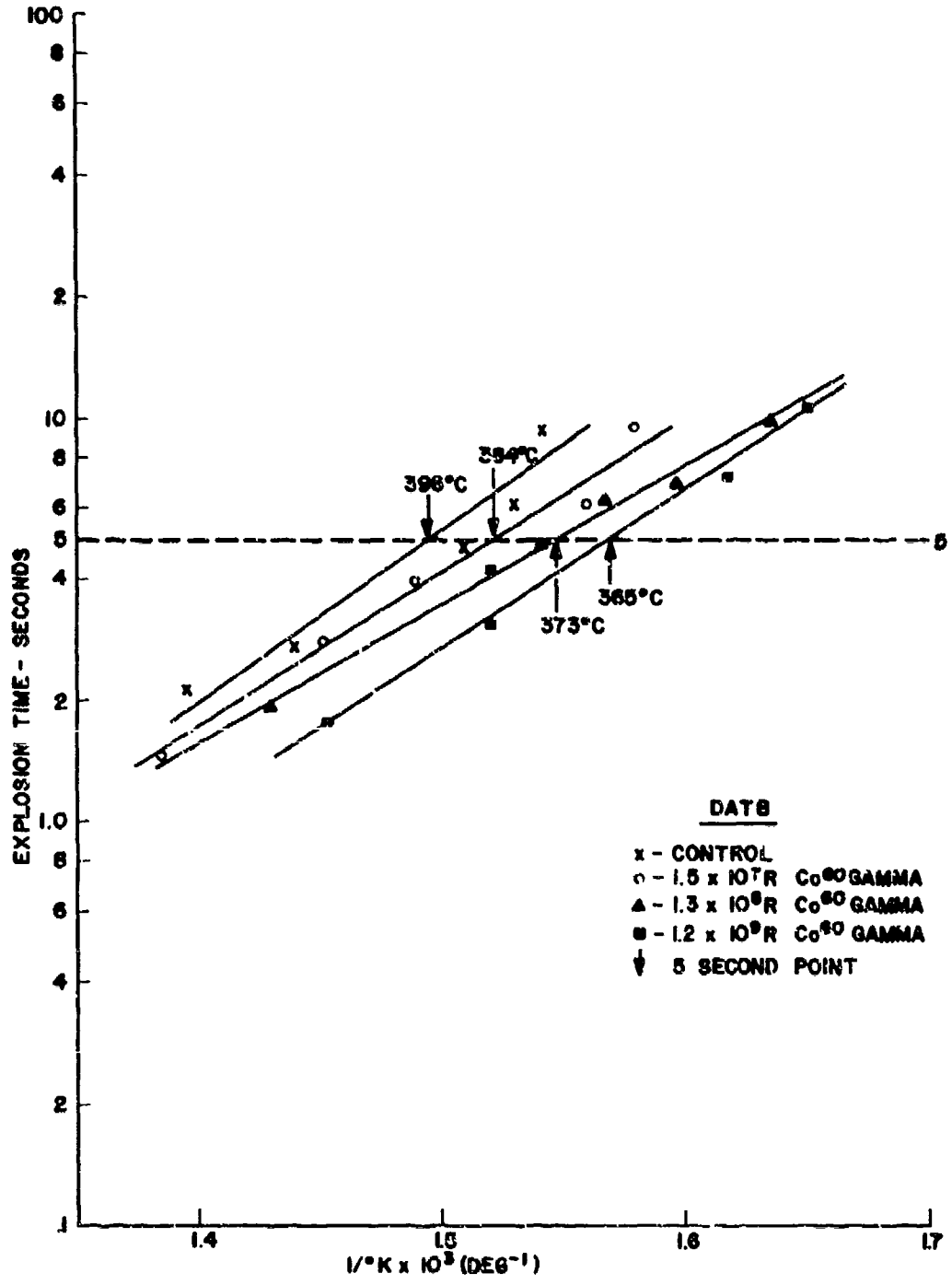

FIGURE 17 Explosion Temperature Curves for DATB Before and After Gamma Irradiation

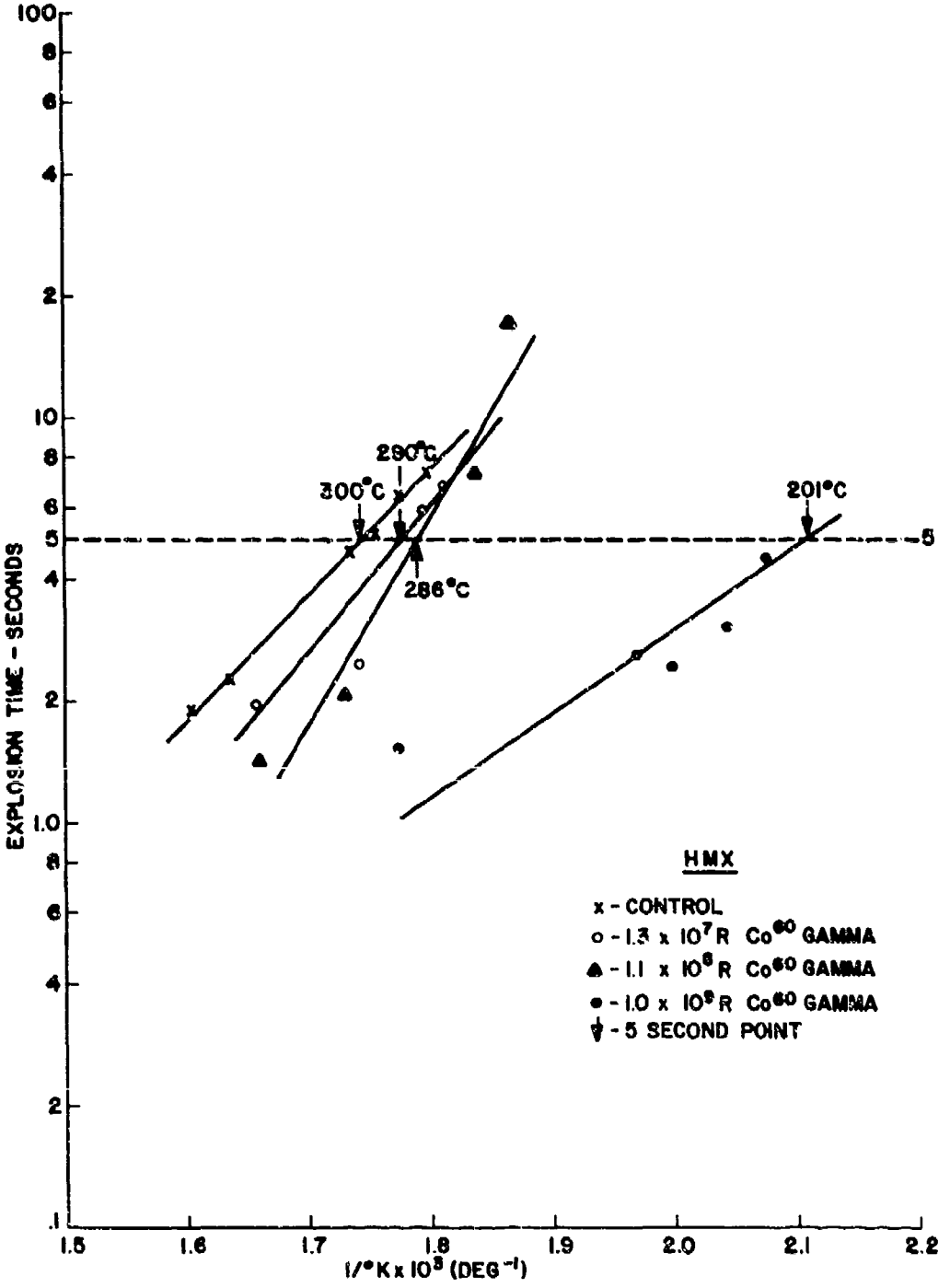

FIGURE 18 Explosion Temperature Curves for HMX Before and After Gamma Irradiation

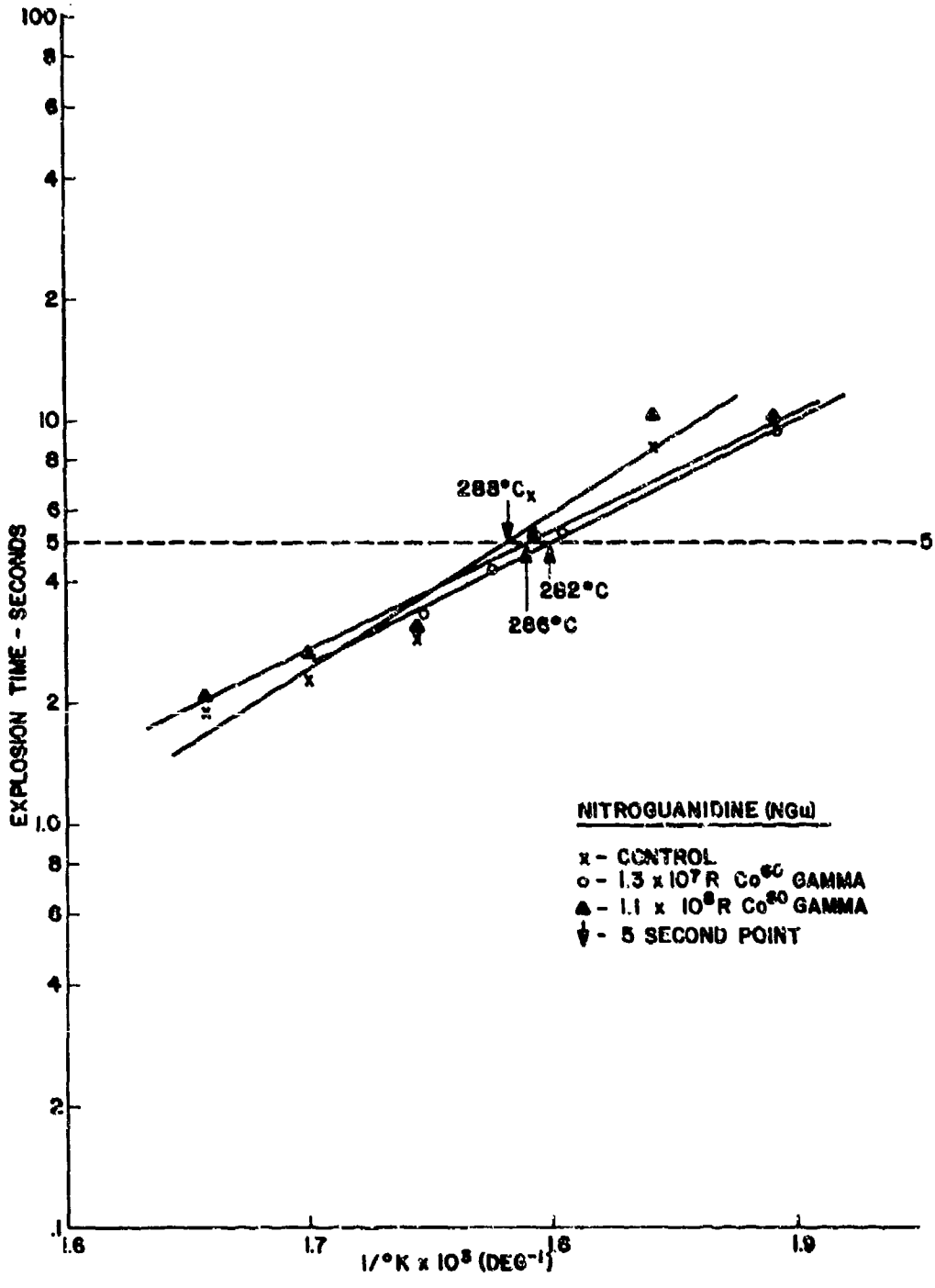

FIGURE 19 Explosion Temperature Curve for Nitroguanidine (NGu) Before and After Gamma Irradiation

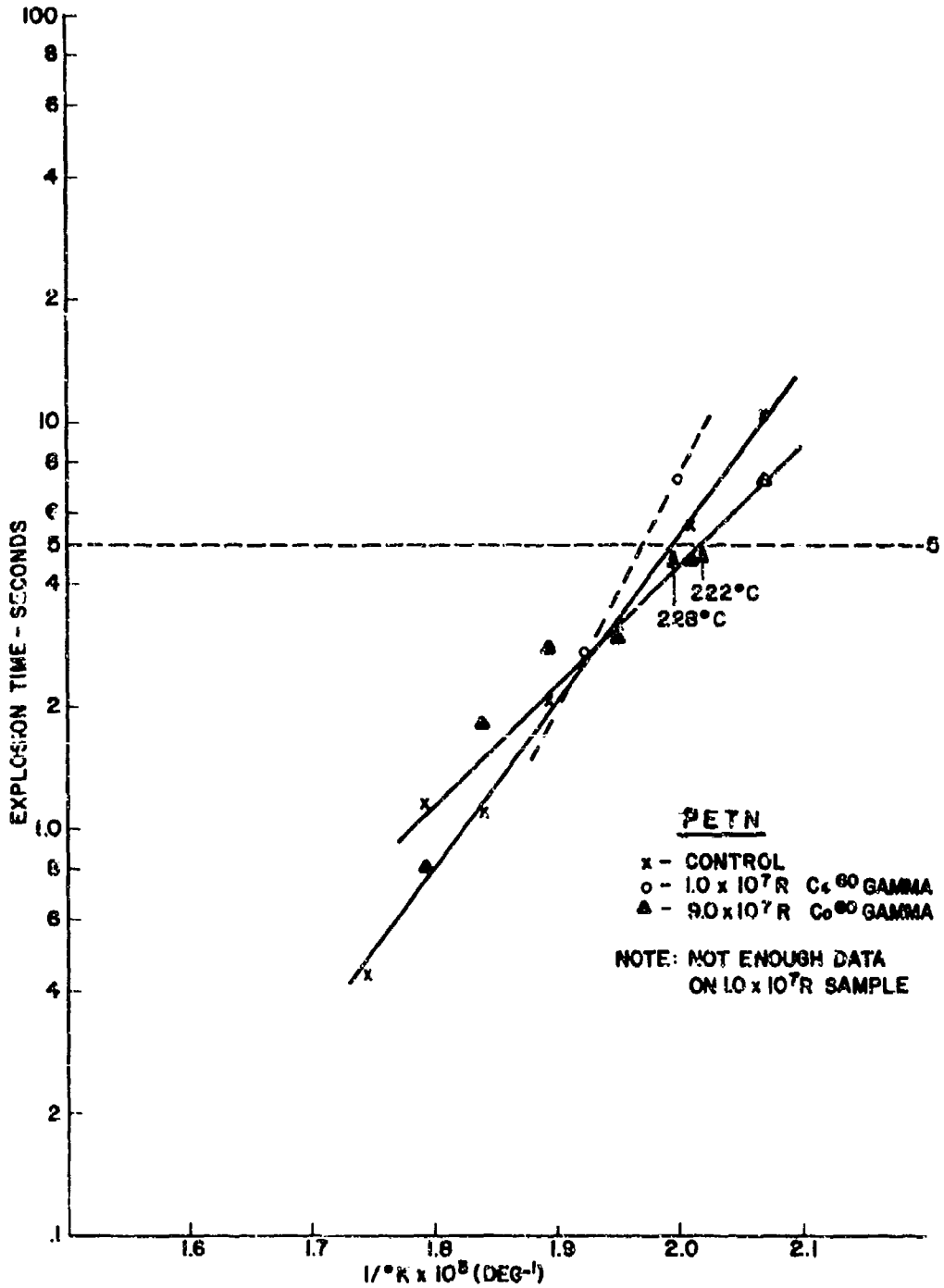

FIGURE 20 Explosion Temperature Curves for PETN Before and After Gamma Irradiation

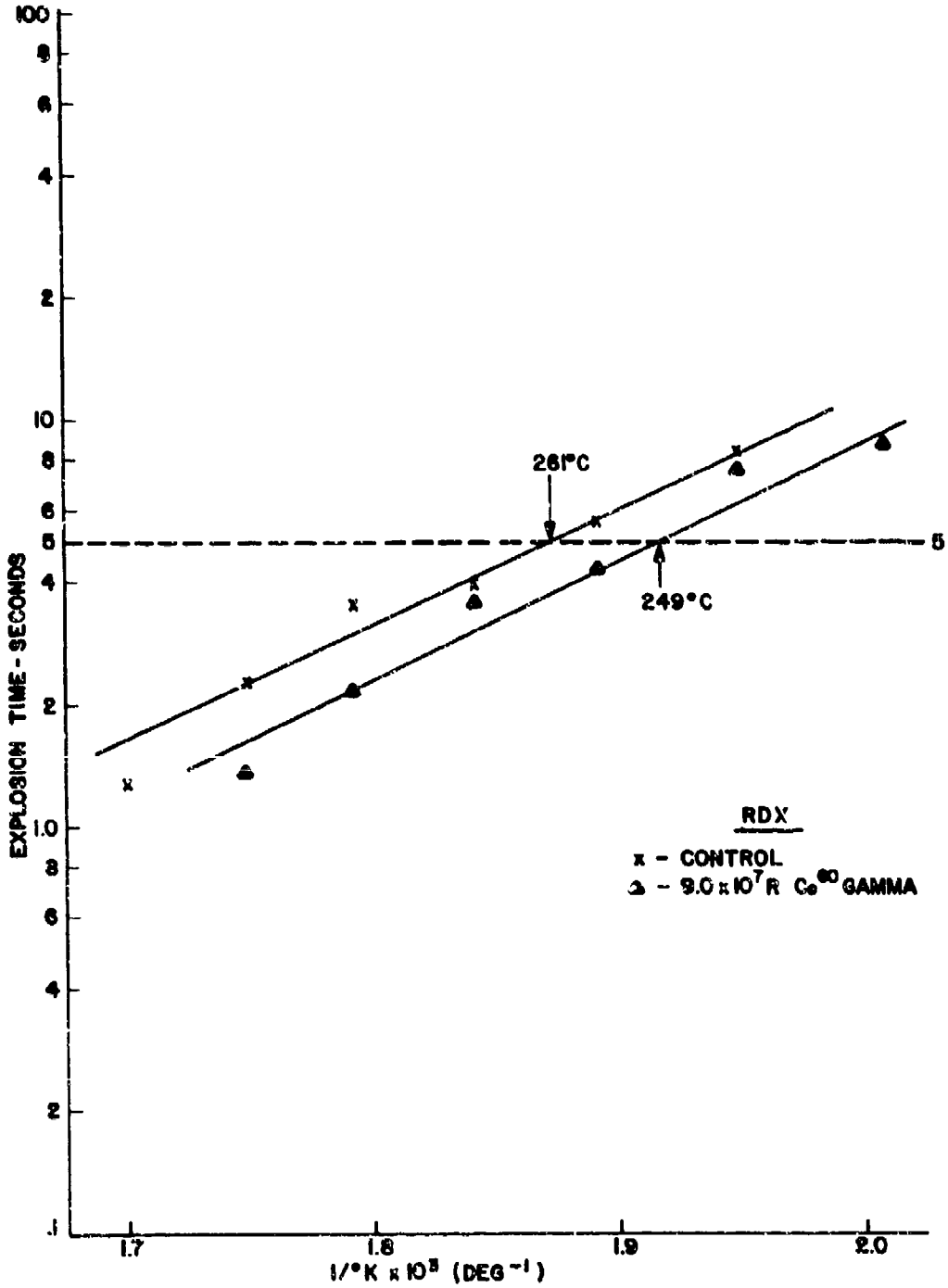

FIGURE 21 Explosion Temperature Curves for RDX Before and After Gamma Irradiation

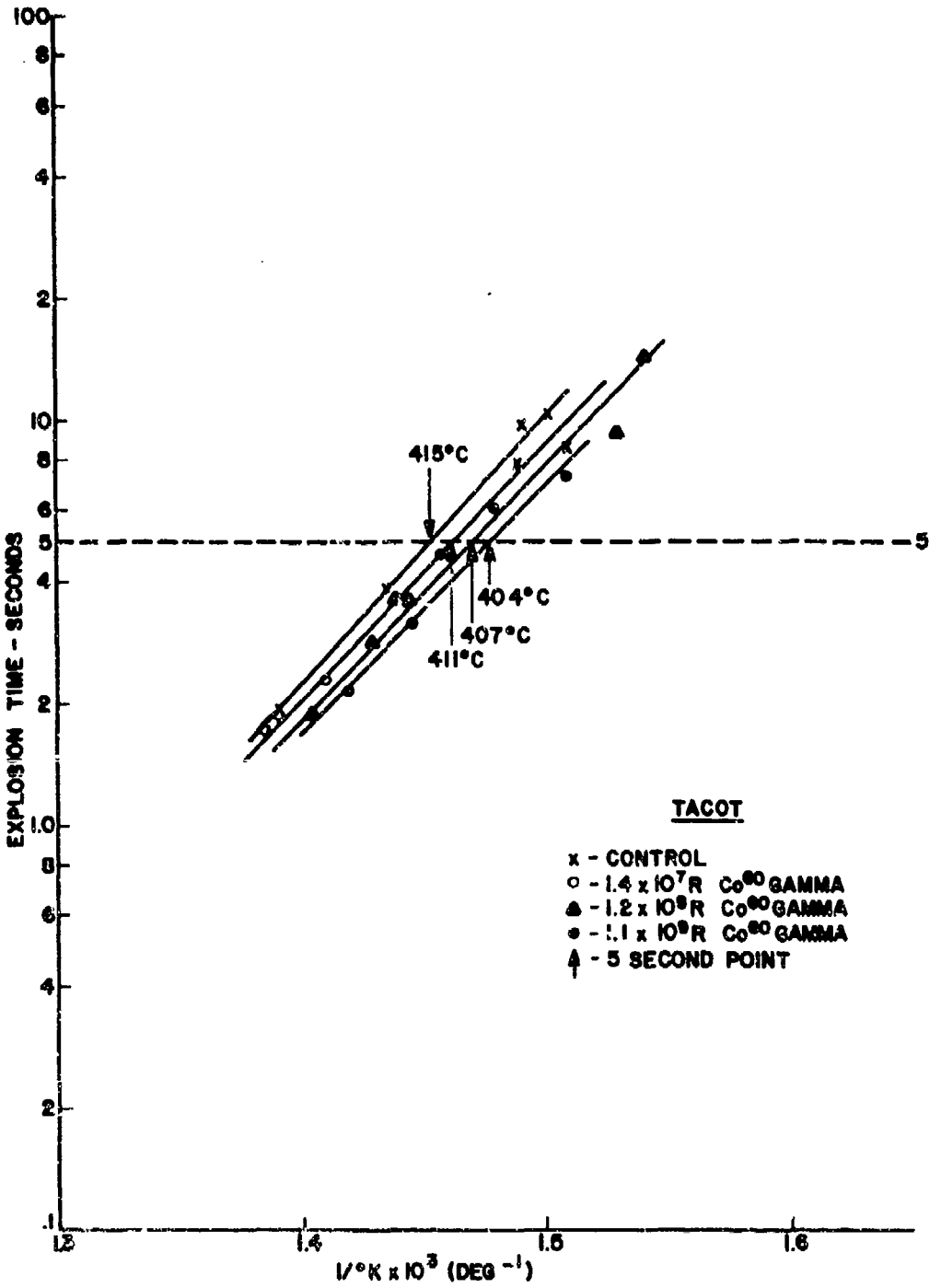

FIGURE 22 Explosion Temperature Curves for TACOT Before and After Gamma Irradiation

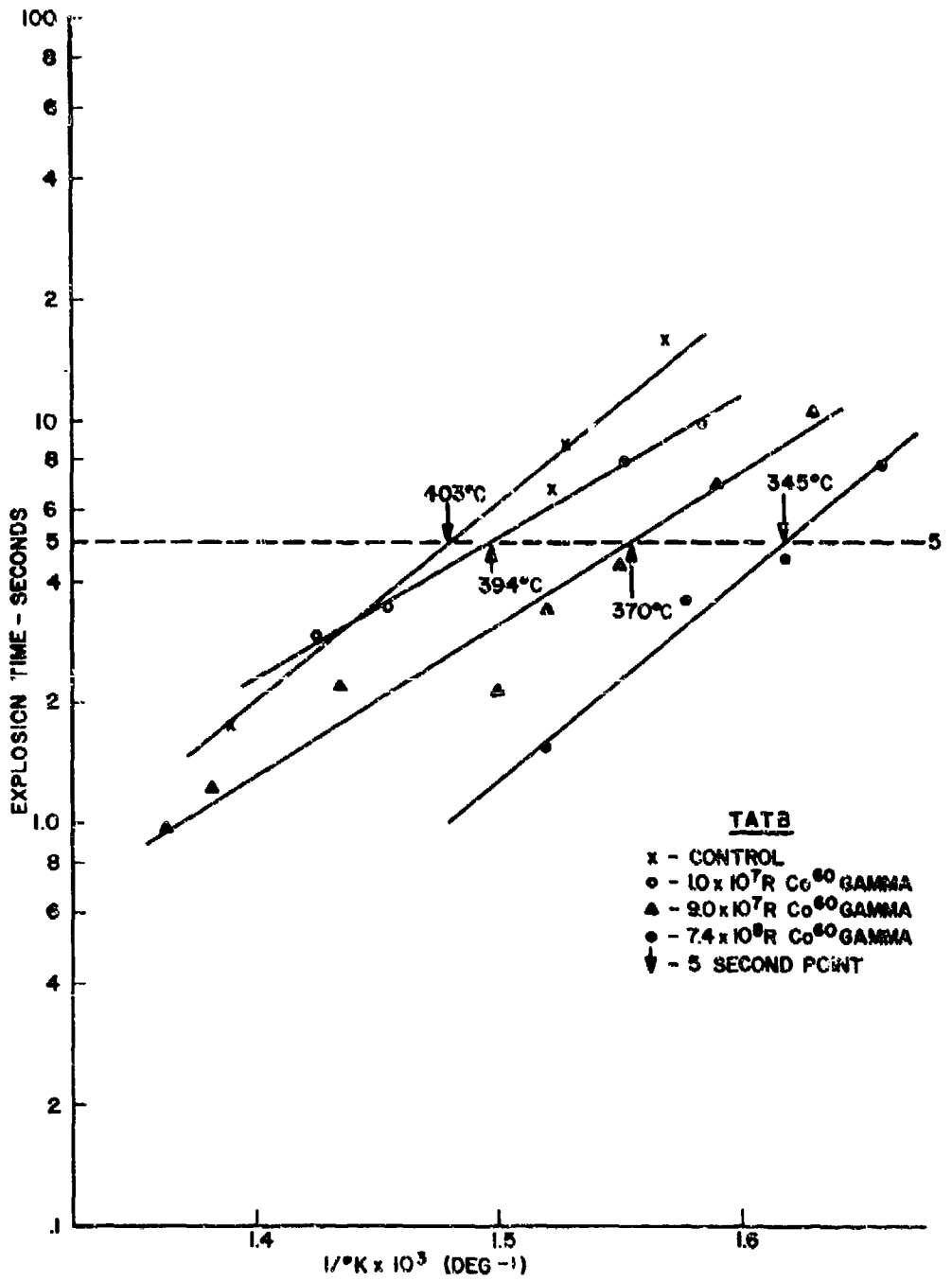

FIGURE 23 Explosion Temperature Curves for TATB Before and After Gamma Irradiation

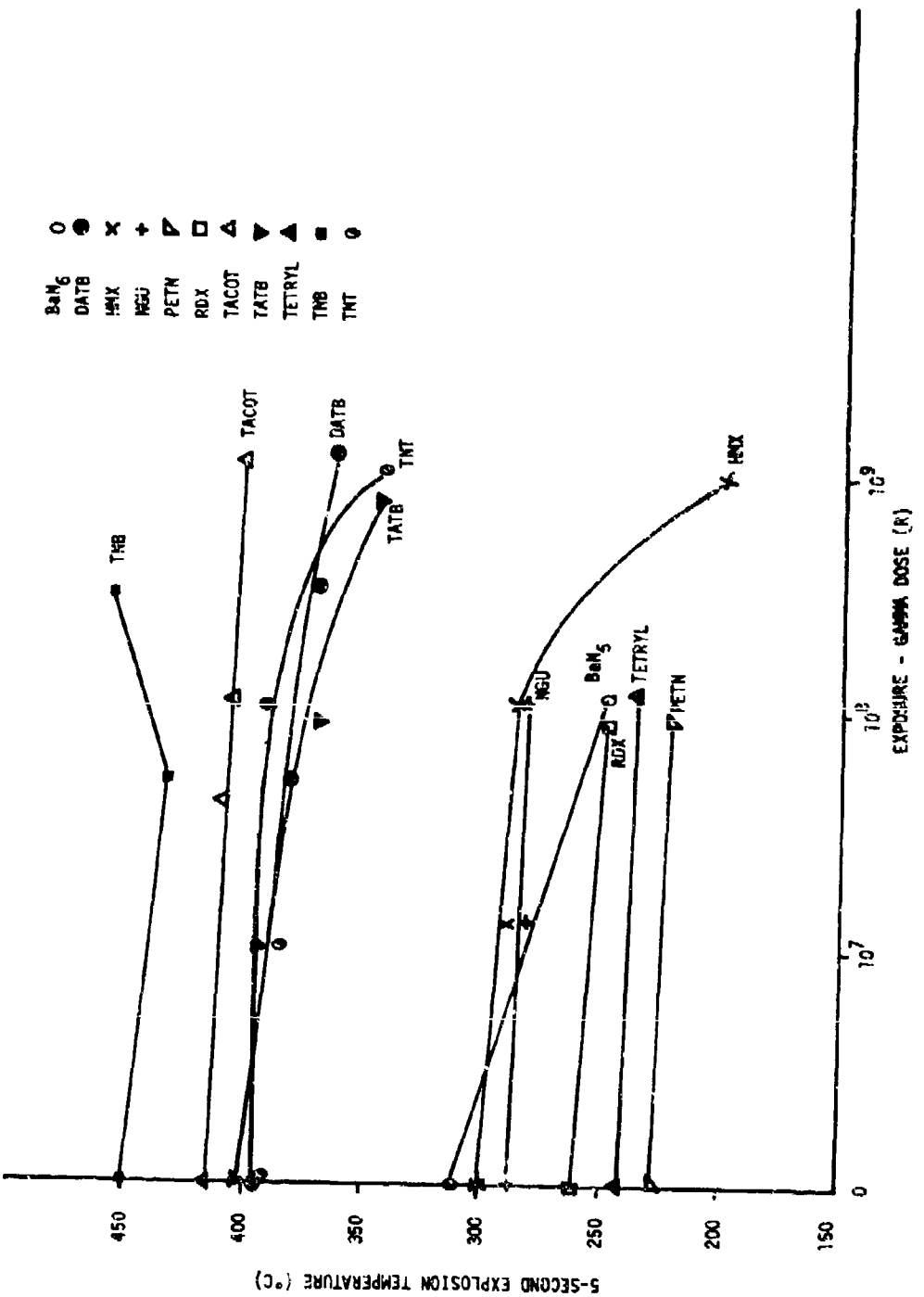

FIGURE 24 Explosion Temperature Curves for Tetryl Before and After Gamma Irradiation

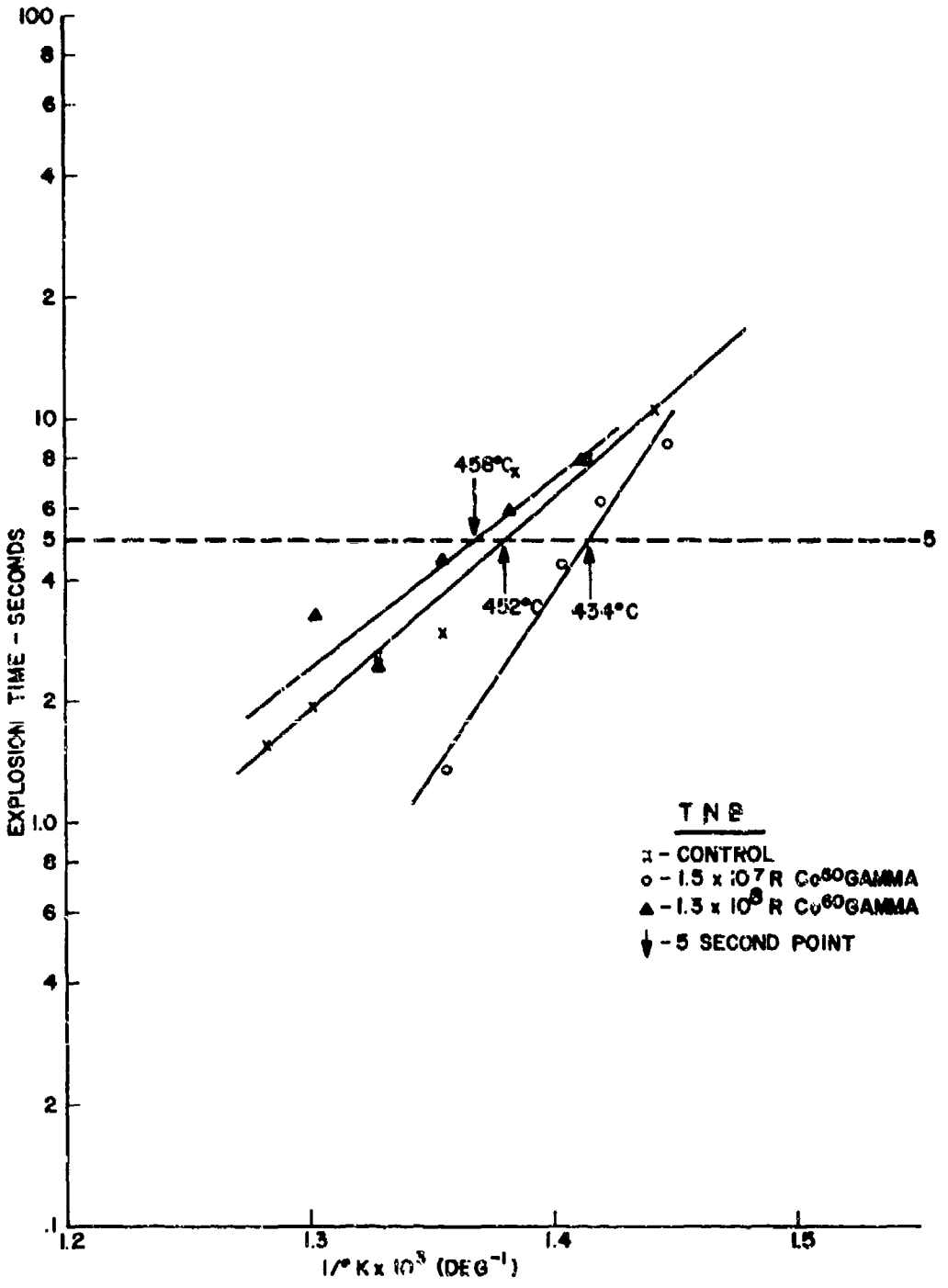

FIGURE 25 Explosion Temperature Curves for TNB Before and After Gamma Irradiation

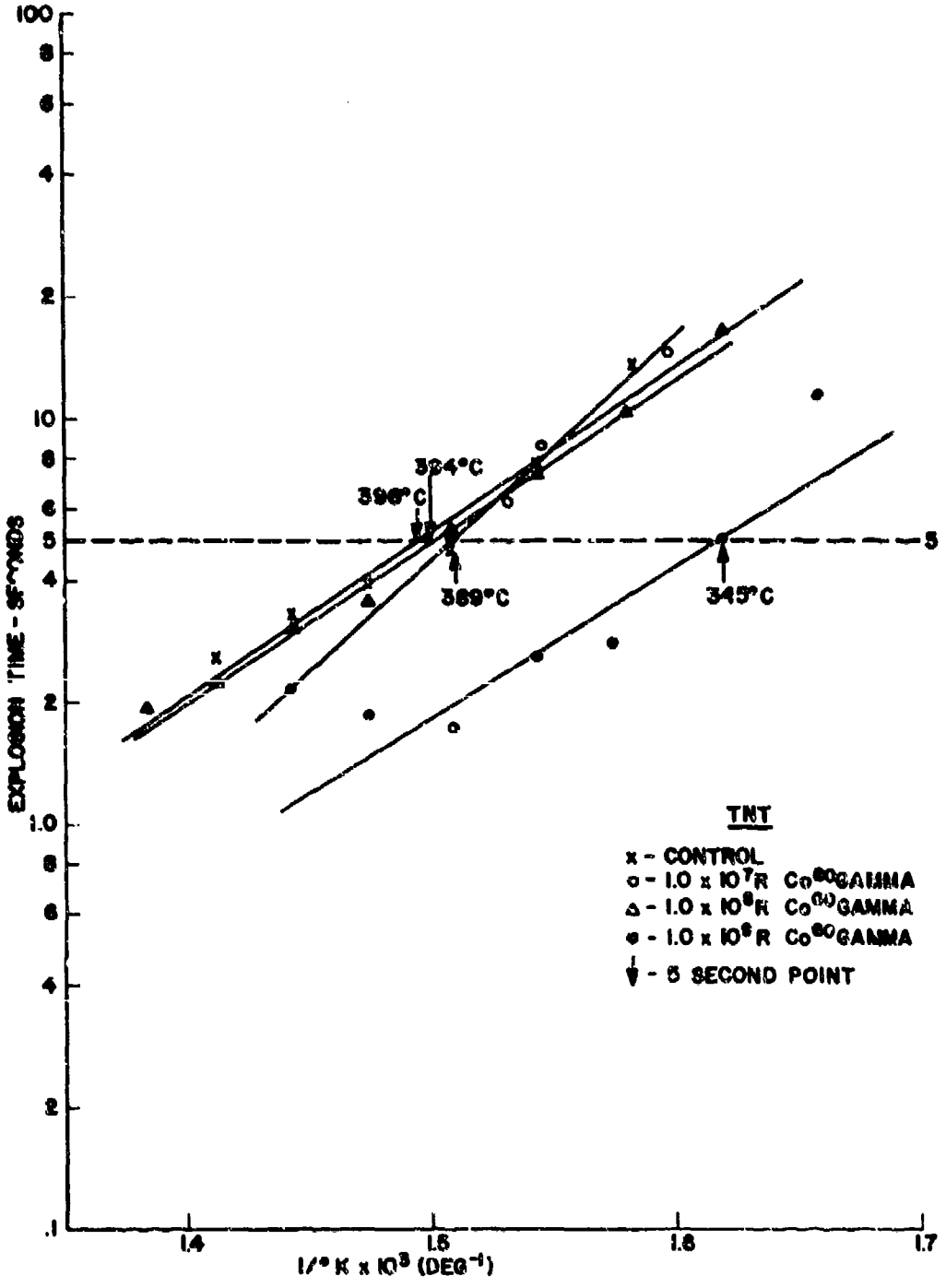

FIGURE 26 Explosion Temperature Curves for TNT Before and After Gamma Irradiation

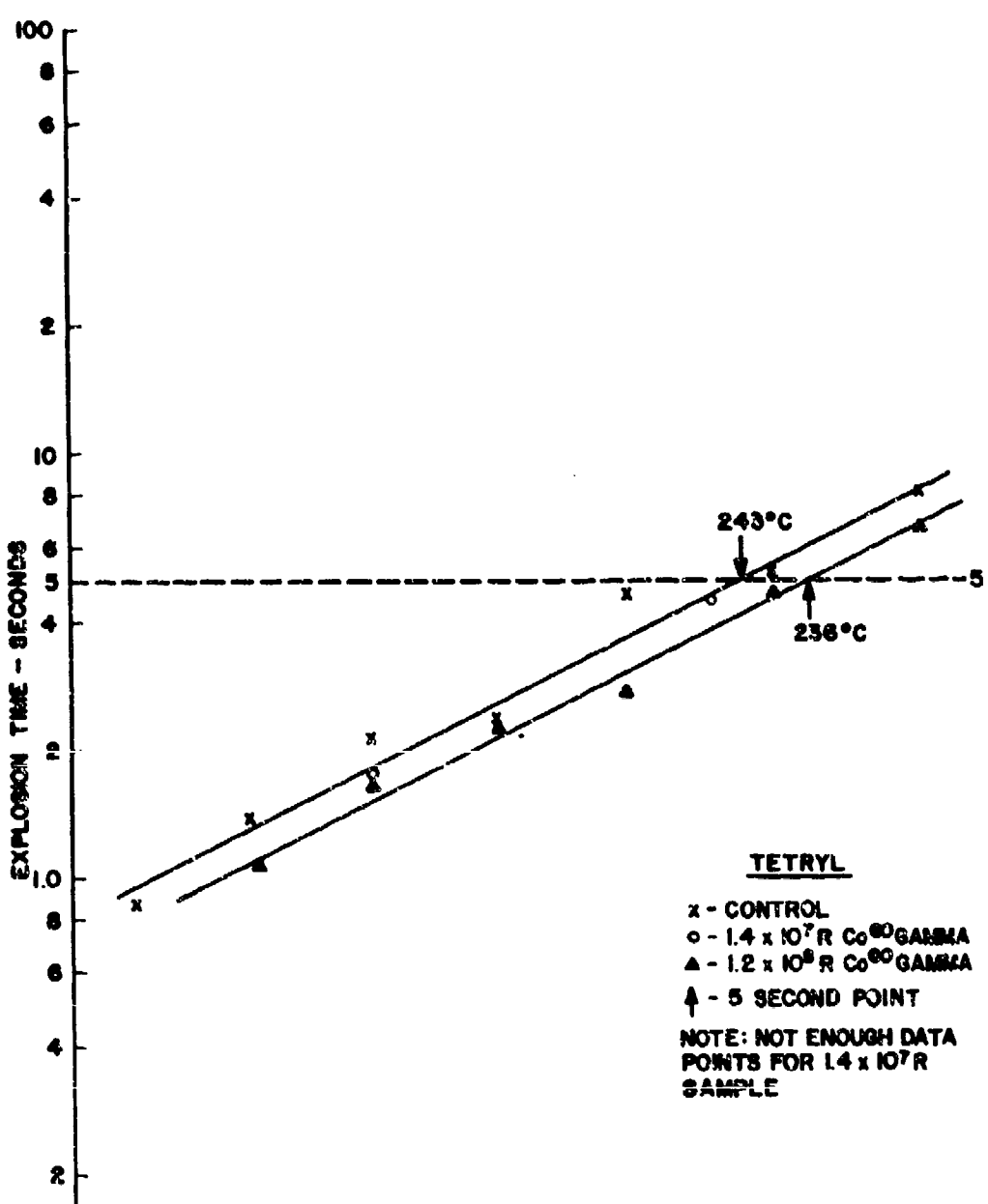

FIGURE 27 Effect of Gamma Radiation on 5-Second Explosion Temperature

The rate stick consisted of approximately eight 1/2-inch diameter, 3/4-inch long explosive pellets in a row and held together by end plates. Each pin was made up of two 0.0003-inch strips of silver foil placed between each explosive increment with the foil ends separated by a 1/16-inch gap. A pair of five copper wires connected each pin to the signal mixer circuit, a network of capacitors and resistors. An array is shown in Figure 28. As the detonation wave passes through the explosive charge the electric pulses are picked up on the master scope. The events are recorded on film and the rates of detonation are computed from the explosive increment lengths and the time measurement displacements on the film.

Figure 29 illustrates the effects of Co^{60} gamma radiation on the rates of detonation with the results listed in Table 8. The irradiated pellets were the samples used to determine the changes in weight loss and dimensions in Table 2. Since BaN_6 could not be detonated, pellets of this material were not irradiated.

Since the densities and detonation velocities were available at the various irradiation levels the detonation pressure was approximated by using the hydrodynamic relationship

$$P = \rho D u \tag{3}$$

which defines the detonation pressure P in terms of the loaded density ρ, the detonation velocity D, and the particle velocity u, for stable detonations. For solid C-H-N-O explosives the approximation

$$u = \frac{D}{4} \tag{4}$$

has been found to be useful. Substituting (4) in (3)

$$P = \frac{1}{4} \rho D^2 \tag{5}$$

When ρ is expressed in g/cc and D in cm/μsec, P is in units of megatons. The values obtained with (5) generally show good agreement to within 10% of measured detonation pressures[1]. The calculated detonation pressures are listed in Table 8 while a plot of the detonation pressure versus density is shown in Figure 30.

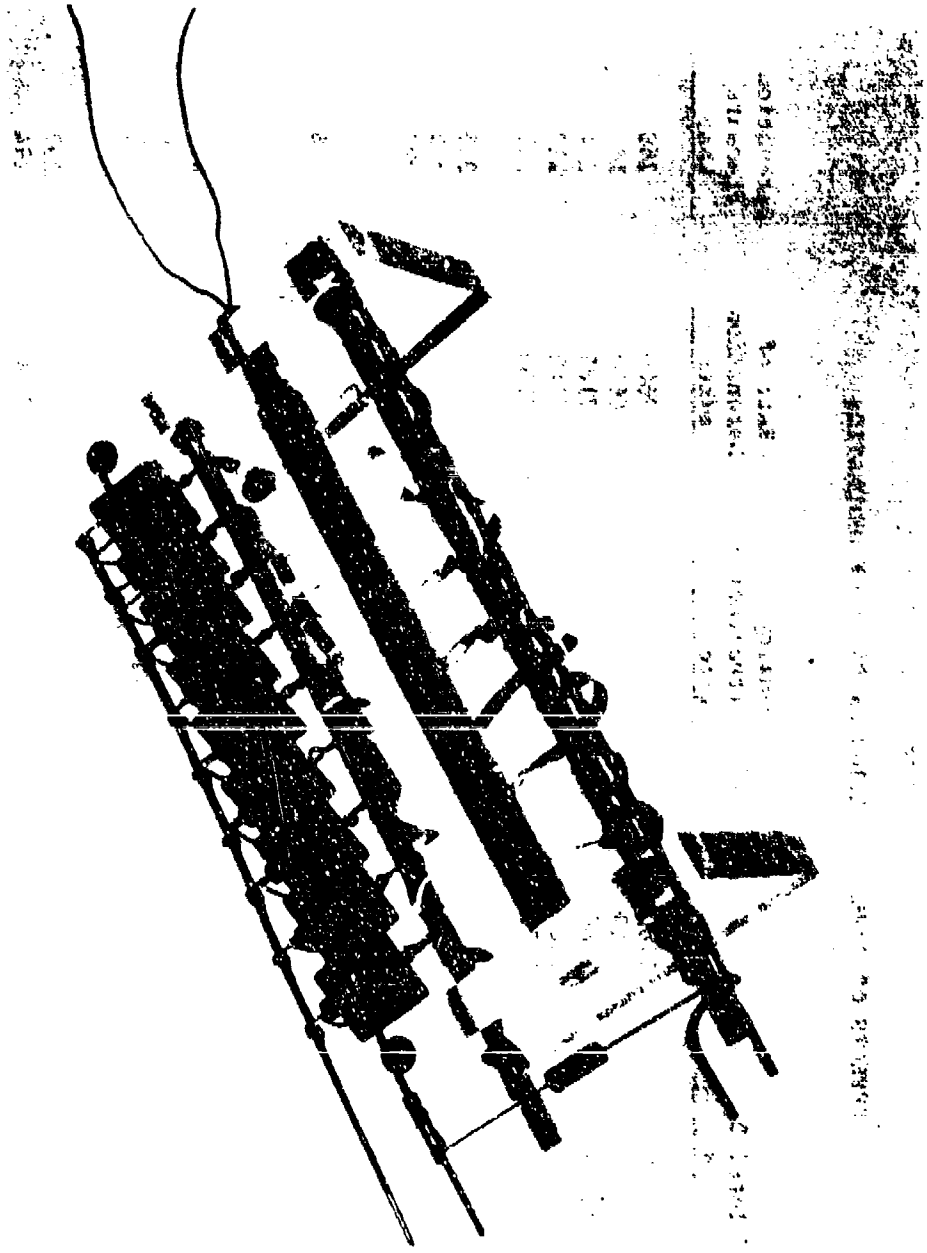

FIGURE 28 Detonation Velocity Test Array

TABLE 8

EFFECTS OF GAMMA RADIATION ON RATES OF DETONATION

Explosive	Total Dose R	Density g/cc	Density After Irradiation g/cc	Rate of Detonation m/sec	Detonation Pressure kbar
DATB	0	1.80	—	7600	260
	0	1.49	—	6630	164
	1.1×10^7	1.66	1.66	7185	214
	1.3×10^8	1.66	1.65	7180	213
	1.1×10^9	1.71	1.70	7235	218
HMX	0	1.75	—	8620	325
	$.1 \times 10^7$	1.75	1.75	8620	325
	3×10^8	1.74	1.66	8410	293
	1.1×10^9	Pellets Crumbled			
NQ	0	1.54	—	7485	216
	1.3×10^7	—	156	Would Not Detonate	
	1.1×10^8	Pellets Crumbled			
PETN	0	1.67	—	8045	270
	1.0×10^7	1.68	1.67	8035	270
	9.0×10^7	1.66	1.54	7660	226
	1.0×10^9	1.66	Pellets Crumbled		
RDX	0	1.69	—	8380	297
	1.0×10^7	1.70	1.68	8360	294
	1.0×10^8	1.70	Very Fragile	6935	—
	1.0×10^9	Pellets Crumbled			

TABLE 8 (Continued)

Explosive	Total Dose R	Density g/cc	Density After Irradiation g/cc	Rate of Detonation m/sec	Detonation Pressure kbar
TACOT	0	1.58	--	6935	190
	1.1×10^7	1.57	1.57	6915	188
	1.3×10^8	1.56	1.56	6910	186
	1.1×10^9	1.38	1.38	6285	136
TATB	0	1.84	--	7510	260
	1.1×10^7	1.84	1.84	7520	260
	1.3×10^8	1.85	1.84	7525	261
	1.1×10^9	1.82	1.81	7435	250
Tetryl	0	1.69	--	7540	240
	1.1×10^7	1.69	1.69	7515	239
	1.3×10^8	1.65	1.62	7400	222
	1.0×10^9	1.62	1.47	7010	181
TNB	0	1.65	--	7150	211
	1.0×10^7	1.65	1.63	7115	206
	1.0×10^8		Pellets Crumbled		
TNT	0	1.60	--	6875	189
	1.0×10^7	1.60	1.60	6875	189
	1.0×10^8	1.59	1.55	6850	182
	1.0×10^9	1.57	1.45	6395	143

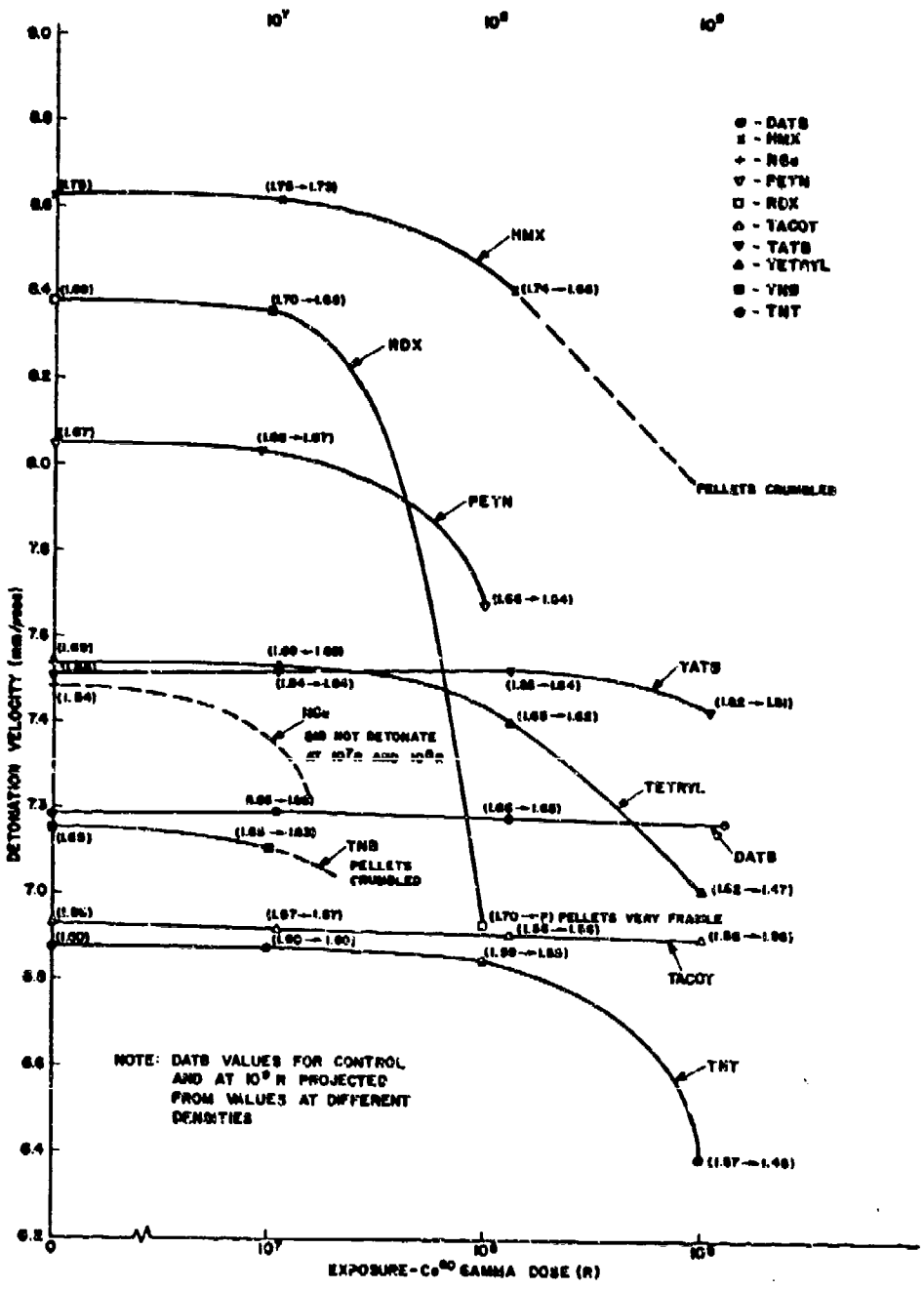

FIGURE 29 Effect of Gamma Radiation on the Detonation Velocity of Explosives

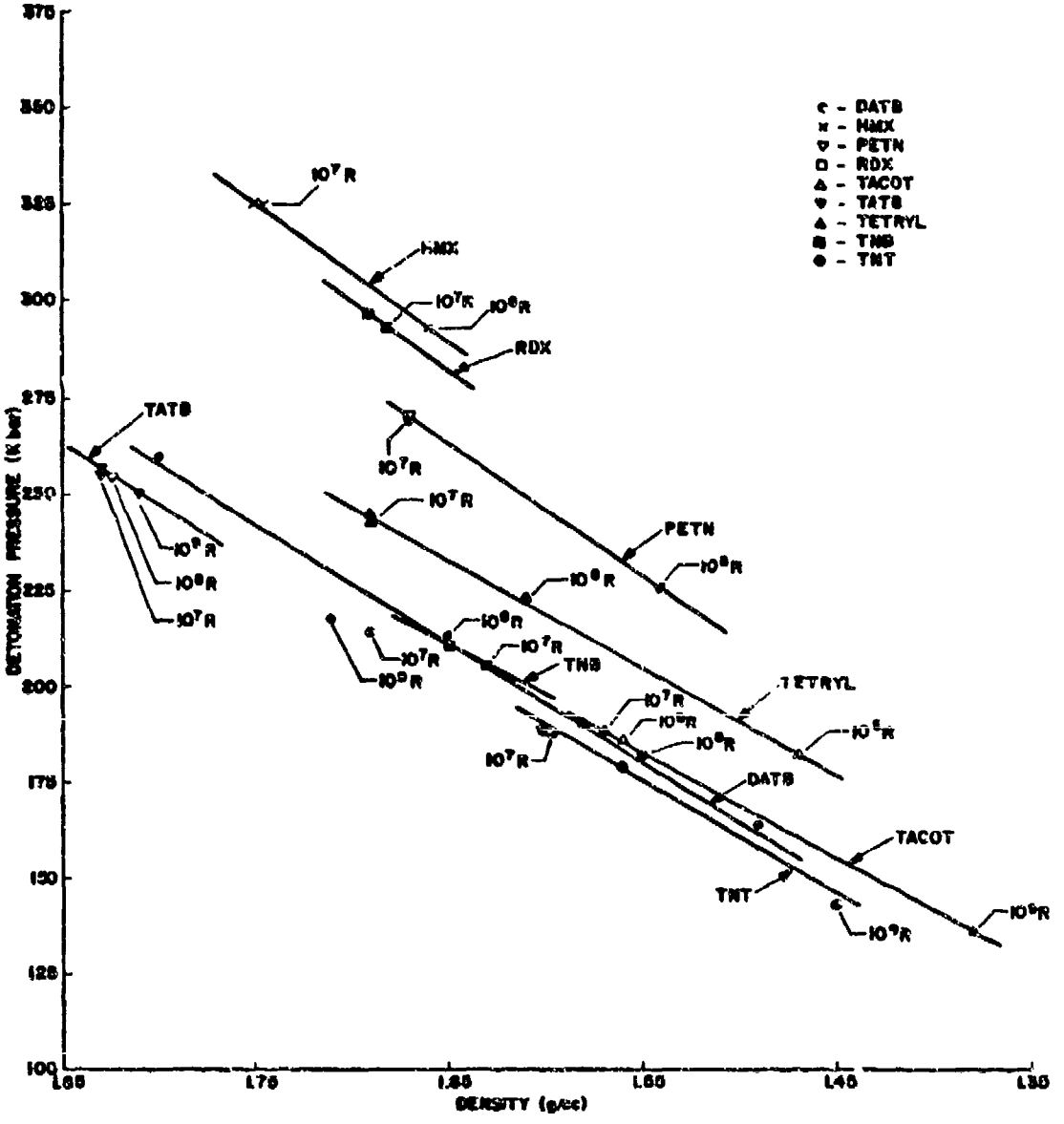

FIGURE 30 Detonation Pressure Versus Density for Explosives Before and After Gamma Irradiation

RESULTS AND DISCUSSION

In evaluating the effects of Co^{60} gamma radiation on the explosives studied in this program the changes in the properties of each explosive were first examined as a function of total dose. The total gamma radiation threshold was then determined. These threshold values were compared with each other so that a determination, or rather an ordering, could be made of the explosives which indicated the ability to withstand gamma radiation.

Comparisons also were made with results reported by other investigations.[8,9,10,11] These will be noted below when the radiation-induced changes are discussed for each material. The reactive materials are listed in the order of their ability to withstand gamma radiation.

It should be pointed out with regard to the detonation rate tests that the values obtained with the irradiated samples, based on their total gamma doses, show that the detonation pressure is a linear function of the density. However, in this work it was not possible to establish clearly whether the observed changes in detonation velocity and density were strictly a consequence of radiation or possibly a consequence of a secondary thermal reaction caused by the gamma radiation. The slopes of all the explosives were quite similar although for RDX and TNB they were based on only two data points. It is to be noted that detonation pressures, calculated from literature values of rates of detonation and densities, fell fairly close to their respective slopes in Figure 30. (This is for densities other than those tested as controls.)

a. TACOT

This high-temperature heat-resistant explosive displayed excellent radiation-resistant characteristics in a gamma environment. When exposed to 3.7×10^9 R TACOT easily passed the 200°C VST. In the weight loss measurements (Figure 2) the powder sample exposed to 1.2×10^8 R indicated a greater loss than the 1.1×10^9 R sample. It is believed that some moisture was introduced to this sample and DATB which caused the varying loss in weight. However, the pellets indicated a very minimal change (>1%) to exposures up to 1.1×10^8 R.

The DTA thermograms for TACOT are shown in Figure 10. Most of the control traces conducted at a heating rate of 20°C/min. resulted in a detonation near the peak of the exotherm (398°C). The

only trace that did not indicate a runaway reaction is shown as the control trace in Figure 10. In order to obtain a complete trace consistently the heating rate had to be reduced to 2.5°C/min. with the onset of the exotherm at 340°C and the peak at 376°C. TACOT does not exhibit an endotherm.

All of the irradiated samples of TACOT resulted in a detonation near the peak of the exotherm. Little change occurred until the TACOT sample was exposed to levels of 1.1 and 3.7 x 10^9R. The exotherm at both levels was shifted downwards resulting in detonations at 385°C and 387°C, respectively. At the highest exposure the onset of the exotherm began at 320°C.

TACOT displayed good thermal stability according to the TGA thermograms. The highest level of exposure (7.0 x 10^9R) produced a 10% weight loss temperature of 330°C. For exposures up to and including 1.1 x 10^9R the 10% value was not obtained since the material deflagrated at 406°C for the control sample and 387°C for the irradiated sample. The TACOT exposed to 3.7 x 10^9R and 7.0 x 10^9R detonated at 370°C and 355°C, respectively with the 10% weight loss temperatures at 354°C and 330°C. At these two high exposures the effect of gamma radiation was noticable on the thermal stability of TACOT since the start of decomposition was 240°C and 180°C, respectively compared to the control value of 350°C.

TACOT normally decomposes at 390°C in the melting point test. With an exposure of 1.1 x 10^9R this material decomposes at 378°C and turns from a red orange to a reddish-maroon dark brown. The IR spectra did not show any changes due to the gamma exposure. The impact test data shows practically no change in the 50% fire value when the material is exposed up to 1.1 x 10^9R (Table 6). Very consistent results were obtained in the explosion temperature test where the 5-second explosion temperature was lowered only 411°C to 404°C with an exposure of 1.1 x 10^9R. With very little change in the dimensions and weight of the pellets as a function of gamma dose it was not surprising that little change was noted in the detonation velocity tests (Figure 29).

b. TATB

TATB is another aromatic compound that seems to withstand gamma radiation. Very acceptable results were obtained in the 200°C VST with a sample exposed to 2.8 x 10^9R. The dimensional and weight loss measurements seem to parallel those for TACOT and DATB at the same exposure levels (>1%).

As with TACOT, TATB also does not exhibit an endotherm. The DTA thermograms for TATB as shown in Figure 11 depict one exotherm. For the control sample the peak of the endotherm is at 384°C and for exposures of 1.0×10^7R, 9.0×10^7R, 7.4×10^8R and 2.8×10^9R the peak shifted to 377°C, 372°C, 365°C and 363°C, respectively. As can be seen the same effect was noted with the onset of the exotherm.

The TGA results for TATB show that for exposures up to 7.0×10^9R the 10% weight loss temperature decreased from 353°C to 299°C. A significant shift was noted at exposures of 2.8×10^9R and 7.0×10^9R. The start of decomposition was 125°C compared to the control value of 285°C. For the latter exposures those samples detonated at 345°C and 342°C, respectively, while the other samples exposed to levels up to 7.4×10^8R decomposed up to a 77% total weight loss at 405°C. Results for 10°C/min., 50°C/min., and 80°C/min. are listed in Table 4.

At all exposure levels TATB decomposed in the melting point test at 400°C while the color changed from a bright yellow to a blackish green. In the impact test data although the 50° fire point was lowered from 22.16 inches, the irradiated 50% fire point stayed in the range of 17-18 inches for the sample exposed from 1.0×10^7 to 7.4×10^8R. In the explosion temperature test an effect was noted in the 5-second explosion temperature which was lowered from a control 403°C to 345°C for an exposure of 7.4×10^8R. However, in the detonation velocity test, only a 1-2% reduction was evident with the 1.1×10^9R sample from the control.

c. DATB

This high-temperature, heat-resistant explosive was one of the materials studied which withstood exposure levels of gamma radiation up to and above 1.2×10^9R. In the 200°C VST the gas evolved was less than 1 cc for exposures up to 1.2×10^9R and 6.15 cc for 4.0×10^9R. The weight loss for the irradiated pellets was very small and consistent with the results obtained by Berberet for smaller pellets.[11] With the powder sample the weight loss generally was higher as a function of dose with the inconsistent value for the sample exposed to 1.3×10^8R being attributed to moisture.

For DATB minor shifts were noted in the DTA thermograms for exposures up to 1.3×10^8R gamma. In the control sample (Figure 5) two exotherms were evident -- a minor one at 313°C and the major one at 353°C. Some shifting of these exotherms occurred at exposures up to 1.3×10^8R. However, at exposures of 1.2×10^9R and 4.0×10^9R the minor exotherm disappeared and the major (larger) exotherm shifted to 349°C and 343°C, respectively.

The melting point endotherm also shifted downward from 282°C to 276°C and finally to 273°C. As can be seen in Figure 5, the small endotherm at 227°C, which had lowered to 220°C at a level of 1.5 x 10^7 R, gradually broadened as a function of dose. Actually at 4.0 x 10^9 R that endotherm was relocated at 240°C where it had flatened out until it was just discernable.

DATB displayed thermal stability up to 272°C for a 10% weight loss for an exposure of 4.0 x 10^9 R gamma. The TGA thermograms indicated that at the highest exposure 82% of the sample had decomposed at 340°C while 96% of the control had decomposed at 345°C. TGA thermograms were obtained for DATB samples subjected to exposures up to 1.2 x 10^9 R at heating rates of 10°C/min, 50°C/min, and 80°C/min. As expected, experience has shown that the values obtained at lower heating rates were lower and those at higher heating rates were higher when compared to a heating rate such as 20°C/min.

The melting point was only lowered 2°C for a total dose of 1.2 x 10^9 R although in the DTA trace the endotherm was lowered almost 10°C. The color of the explosive darkened from a yellow to a dark, purplish brown from the exposures. The impact test results did reveal a lowering of the 50% point as a function of gamma dose from a control value of 20.64 to 13.50 inches for the highest exposure. The 5-second explosion temperature value was reduced monotonically from 396°C to 365°C as a function of dose with little change in the apparent activation energy. With respect to performance, DATB displayed excellent results since the effect on the detonation velocity was minimal.

d. HMX

The results obtained on HMX as a function of gamma dose strongly indicate that the threshold irradiation level that HMX can withstand is up to 1.0 x 10^8 R. This is borne out by the results from the VST, weight loss, DTA, TGA, melting point, 5-second explosion temperature and the detonation velocity. The most indicative factor was the crumbling of the pellets at the 1.1 x 10^9 R exposure level. For HMX, the highest gamma dose exposure, from which an acceptable, although marginal, 200°C VST value was obtained, was 1.1 x 10^8 R.

The DTA thermograms of the control and irradiated samples of HMX in Figure 6 reveal that the peak exotherm moved upwards to 293°C from 286°C with an exposure of 1.1 x 10^8 R but decreased to 270°C when exposed to 1.0 x 10^9 R. At 1.1 x 10^8 R a small exotherm appears with a peak at 179°C and this also flattened out at 172°C with the increased exposure at 1.0 x 10^9 R gamma.

In the TGA results the 10% weight loss temperature of HMX decreased from 282°C to 185°C as the gamma radiation dose was increased to 1.0×10^9 R. A lower onset of decomposition also was noted. This onset temperature was decreased from the control value of 250°C to 105°C for the 1.0×10^9 R level. In the same range the temperature at which the HMX detonated was lowered from 282°C to 252°C.

The melting point value for HMX did not change significantly until the 1.0×10^9 R level where the material decomposed at 255°C. HMX did not change in color. It remained white up to the level of 1.0×10^9 R.

The impact sensitivity data indicated that HMX becomes more sensitive as a function of dose from a control 50% value of 14.04 inches to 8.96 inches when exposed to 1.1×10^8 R. Although not considered significant, an increase of 1 inch was recorded for the material exposed to a level of 1.0×10^9 R. In the explosion temperature test the 5-second temperature decreased by 14°C to 286°C when subjected to a dose of 1.1×10^8 R (Figure 18). However, at the 1.0×10^9 R level the 5-second explosion temperature value was lowered to 201°C — almost a 100°C reduction (Figures 18, 27). The same type effect was noted in the apparent activation energy values (Table 7). In the detonation velocity tests a definite change of 4.5% was noted in the density at the 1.3×10^8 R exposure level which reduced the detonation velocity from 8620 to 8410 m/sec. The VST, DTA, weight loss, melting point and impact test data were in agreement with results obtained by Berberet[11] and Urizar et al[10], although the latter subjected their samples to a combined neutron and gamma environment.

e. Tetryl

This booster-type aromatic compound produced some erratic results when subjected to gamma radiation. With the VST only the 1.4×10^7 R sample was able to pass the 120°C test while the 1.2×10^8 R sample failed. However, it did pass the 100°C test. This may have been due to its melting point. The weight loss measurements in powder and pellet form increased dramatically from the 1.3×10^8 R to 1.0×10^9 R exposure level.[11]

By the DTA traces tetryl did not show much change until it was subjected to an exposure over 1.2×10^8 R. At 1.05×10^9 R gamma the melting point endotherm had widened and shifted from the control temperature of 128°C to 117°C. From Figure 12 it can be seen that the tall maximum exotherm at 220°C was reduced and broadened with peaks at 195°C and 210°C for the 1.05×10^9 R exposure level and

164°C and 203°C for the 1.44×10^5 R level. For the highest level (1.44×10^5 R) the widened endotherm peaked at 109°C.

With the TGA traces the 10% weight loss temperature of tetryl could not be obtained since the samples had lost only 7-8% when deflagration occurred. Tetryl deflagrated in the range from 215°C to 212°C when subjected to gamma radiation up to 1.2×10^8 R. The onset of decomposition was lowered from the control value of 180°C to 140°C after being exposed to a dose of 1.2×10^8 R. The color changed from yellow to a brownish yellow at the highest exposure. The impact test results, although within a small range (17-19 inches), seem to indicate an erratic behavior. Although the 1.2×10^8 R sample was the only irradiated tetryl subjected to the explosion temperature test, the results were comparable with the control but for a decrease from 243°C to 236°C in the 5-second value. In the detonation velocity tests a density change did not become evident until the sample had been exposed to 1.3×10^8 R where it went from 1.65 to 1.62 g/cc. However, at the 1.0×10^9 R level the density change was from 1.62 to 1.47 g/cc which lowered the detonation velocity from 7540 to 7010 m/sec.

f. TNB

Two aromatic explosives, TNB and TNT, selected for this program, have relatively low melting points (120°C and 81.5°C, respectively). Of the two TNB displayed more resistance to gamma radiation. TNB produced acceptable results in both the 100°C and 200°C tests although the 1.0×10^9 R sample evolved almost three times as much gas in the 100°C test as the 200°C test. Although the 1.0×10^9 R sample in powder form did not produce much of a weight loss, the pellets were all broken. Also the 1.0×10^8 R sample pellets crumbled upon contact so that the detonation velocity tests could not be performed for these two exposures. The weight loss values agree with the results by Berberet.[11]

TNB does not display any exotherms. Two endotherms characterize its DTA thermogram as shown in Figure 13. The control trace indicated a minor peak endotherm at 121°C and a major one at 353°C. TNB was subjected to Co^{60} gamma radiation exposures as follows: 1.5×10^7 R, 1.3×19^8 R and 1.0×10^5 R. Due to the irradiations, the first endotherm (121°C) shifted to 119°C, 120°C, and 112°C, respectively. The second endotherm became a doublet with peaks at 367°C and 351°C with a dose of 1.5×10^7 R, stayed a doublet with peaks at 356°C and 361°C at 1.3×10^8 R and returned to a single endotherm located at 349°C with an exposure of 1.0×10^9 R.

TGA thermograms were obtained for TNB which had been subjected to exposures up to 1.0×10^9 R gamma. The 10% weight loss temperature ranged from 218°C to 180°C for the irradiation noted. The traces also indicated that 95-97% of these samples were decomposed at 285°C for the control and 245°C for the sample which received 1.0×10^9 R. The results for TNB samples heated at 10°C/min, 50°C/min, and 80°C/min. are listed in Table 4.

The highest exposure, 1.0×10^9 R, produced a color change from pale yellow to brown and the melting point was lowered from 120°C to 113°C. The 50% impact test results changed from 23.26 inches for the control down to 18.5 for the 1.4×10^7 R sample, back up to 20.5 for the 1.2×10^8 R sample and then up further to 32.5 for the 1.0×10^9 R sample. The 5-second exposure temperature shifted down from 452°C to 434°C for the 1.5×10^7 R sample and then back up to 458°C for the 1.3×10^8 R sample. This cannot be explained at this time. With the detonation velocity results only the lowest radiation exposure was tested and this did not produce any change.

g. TNT

TNT has the lowest melting point of any explosive in this study. The VST was conducted only at the 100°C temperature and TNT produced acceptable results at the 1.0×10^9 R exposure level. The weight loss of the pellets, which showed a definite increase as a function of dose, agreed with the results by Berberet[11] for exposure up to 1.0×10^8 R. The DTA traces start showing definite changes at the 1.0×10^8 R level which increase at the 1.0×10^9 R level.

The TNT DTA thermograms are depicted in Figure 14. The control DTA trace indicates a peak endotherm at 81°C and a peak exotherm at 324°C. As a function of gamma radiation both of these peaks were lowered in temperature. At 1.0×10^7 R the endotherm stayed at 81°C while the exotherm peaked at 321°C. At 1.0×10^8 R the endotherm became a doublet with peaks at 78°C and 79°C while the peak of the exotherm was relocated at 315°C. At the highest dose, 1.0×10^9 R the endotherm widened almost from the start of the trace with a peak at 71°C and the exotherm had shifted to 290°C.

For TNT TGA thermograms were obtained for exposures up to 1.0×10^9 R. The 10% weight loss temperature decreased from 190°C for the control value to 173°C for the 1.0×10^9 R exposure. For the control sample 99% of the material had decomposed at 250°C while for the 1.0×10^9 R sample 86% of its weight was lost at 235°C.

The impact data implies that TNT became less sensitive as a function of gamma dose going from a 50% value of 25.5 inches to 30.11 inches for the 1.0×10^9 R level. The 5-second explosion temperature value did not change very much when exposed to 1.0×10^8 R but at the 1.0×10^9 R level the value went from 396°C to 345°C. In the detonation velocity test a slight change was evident at the 1.0×10^8 R level but a significant effect occurred with the 1.0×10^9 R sample where the density of that material was lowered from 1.57 to 1.45 g/cc and the velocity was reduced from 6875 to 6375 m/sec.

h. RDX

Compared to HMX, RDX was affected the most, based on the exposures to which these materials were subjected. In the VST the only acceptable results were obtained with the 1.0×10^7 R sample and this was only with the 100°C test. In the weight loss measurements the RDX pellets which had been subjected to 1.0×10^8 R became very soft and crumbled on contact, giving off a strong odor. Berberet[11] and Urizar[10] reported the same type of results.

Figure 9 depicts the DTA thermograms for RDX. The control DTA showed a double endotherm with peaks at 193°C and 197°C. When exposed to a gamma dose of 1.0×10^7 R one of the endotherms disappeared with the other peaking at 194°C. At an exposure of 9.0×10^7 R the other endotherm reappeared at 184°C while the major endotherm remained at 194°C. However, with a total dose of 1.06×10^9 R the endotherm widened indicating only one peak at 190°C.

The TGA results obtained for RDX showed some pronounced effects and they did not follow the same trend as HMX. The 10% weight loss temperature for RDX was lowered drastically from 230°C for the control to 63°C for a RDX sample exposed to 9.0×10^7 R gamma. In each case the material deflagrated or detonated at 240°C. For those samples the start of decomposition occurred at 190°C and 38°C, respectively, which indicated a significant change caused by the gamma radiation.

The RDX exposed to 1.06×10^9 R became a white paste and decomposed at 191°C in the melting point test.[10] The impact test data indicated an increase in sensitivity at the 9.0×10^7 R which does not agree with Urizar[10] at about the same level. The different type impact test may be part of the answer. At the same exposure level the 5-second explosion temperature was reduced from 261°C to 249°C with little change in the slope. The detonation velocity was not affected at the 1.0×10^7 R level but at the 1.0×10^8 R level the RDX pellets were so fragile that the density and weight measurements were not

made. The pellets were assembled and a detonation velocity of 6935 m/sec was obtained which was a significant decrease.

1. PETN

PETN was the other aliphatic compound besides NGu studied in this program. Although the effect of gamma radiation was not as drastic in the detonation velocity results as NGu, the results still indicated that the material undergoes a very significant change under any amount of radiation. In the VST, PETN could only pass the 100°C test with the minimum exposure of 1.0×10^7 R. Both in the powder and pellet form definite effects were noticeable in the weight loss measurements. The pellets swelled and the weight loss at the 9.0×10^7 R level was the highest of any of the other explosive pellets (7.1%).

In the DTA thermogram for PETN the effects of gamma radiation at levels up to 9.0×10^7 R as shown in Figure 8 were slight. The peak exotherm had not shifted and the peak endotherm had widened and moved from 143°C to 138°C. Although the DTA thermogram for the 1.06×10^9 R sample was not perfectly horizontal, it did indicate that the endotherm had disappeared and that two broad exotherms were evident at 163°C and 242°C.

The TGA traces for PETN subjected to levels up to 9.0×10^7 R and the control sample indicated that about 96% decomposition occurred at 220°C. Although the 10% weight loss temperature reduced from 187°C to 177°C, the important part is that the onset of decomposition did decrease drastically from 160°C for the control sample to 70°C for a dose of 9.0×10^7 R. When the samples were run at a heating rate of 50°C/min. the trend remained the same, but all of the sampled deflagrated in the range from 219°C to 212°C.

The 9.0×10^7 R exposure produced a 5°C shift to a lower temperature for the melting point and the 1.06×10^9 R sample was reduced to a white paste. The results for the VST and melting point were consistent with those reported by Rosenwasser[8] and reviewed by Kaufman[9] although the energy of the gamma radiation used in that study was one-third of the gamma energy of the program. In addition the weight loss results of Urizar et al[11] at the integrated flux level which included a 2×10^8 R gamma component were in agreement with the results at the corresponding exposure. The impact test results were erratic. Although the 9.0×10^7 R sample indicated only a reduction of 2 inches in the 50% fire point the standard deviation was very large. The 1.06×10^9 R sample was not impact tested because it was pasty and stuck in the vial. Only the 9.0×10^7 R sample was

tested in the explosion temperature test and the 5-second temperature and the apparent activation energy indicated a downward trend. In the detonation velocity tests the significant changes in the diameter and weight loss affected the detonation velocity for the 9.0×10^7 R sample to be reduced from the contest 8045 m/sec to 7660 m/sec. All the pellets irradiated at the 1.06×10^9 R level crumbled.

j. Nitroguanidine (NGu)

The aliphatic compound NGu did not display much resistance to gamma radiation. The most drastic and permanent effect was shown when the pellets irradiated to a level of 1.3×10^7 R would not detonate in the detonation velocity test although only a 0.4% weight loss was noted. In the VST data the material indicated acceptable results in the 120°C test to exposures up to 1.1×10^8 R.

Nitroguanidine was irradiated at different levels up to a total exposure of 1.44×10^9 R gamma. As can be seen in Figure 7 the DTA thermograms indicate that peak exotherm starts from the melting point endotherm at 240°. Both the endotherm and exotherm are lowered in temperature from the effects of gamma radiation. The peak exotherm shifts from the control temperature at 249°C downward to 234°C for a total exposure of 1.44×10^9 R. The endotherm not only shifts in the same direction from 240°C to 226°C but it also becomes shallower.

TGA thermograms were obtained on nitroguanidine (NGu) samples that had been subjected to total doses up to 1.1×10^8 R gamma. Both control and irradiated samples deflagrated in the range from 249°C to 244°C with the 10% weight loss temperature decreasing from 248°C to 231°C.

The melting point did not exhibit much of a change but another effect that indicated substantial desensitization was the fact that in the impact test no fires were recorded at 36 inches for the 1.0×10^9 R sample. In the explosion temperature test the 5-second value did not show a major shift for exposures up to 1.1×10^8 R. This also was reflected in the apparent activation energy. At 1.0×10^7 R and also at 1.0×10^8 R nitroguanidine (NGu) would not propagate when tested.

k. Barium Azide

This inorganic azide, though a reactive material, is not a true explosive. Of all the materials tested, this one was affected the most by the gamma radiation. The VST results show that the material deflagrated in the 200°C test at exposures as low as

1.4×10^7R. When the test was rerun at 100°C for 40 hours an excessive gas evolution was obtained for the sample exposed to 1.2×10^8R. The acceptable value at 100°C, when exposed to 1.0×10^9R, is probably explained by the comparable DTA and TGA thermograms. In the DTA the large exotherm has practically disappeared so the sample may have been only a residue. Actually the IR spectra (Figure 15) indicated that the material was decomposed and subsequently reformed into a form of barium carbonate. This was the only material in which the melting point increased with exposure and with the 1.2×10^8R sample the material exploded at 260°C. The impact test results were erratic but the sample with the highest exposure did not indicate any fires at 36 inches. A definite change was noted in the explosion temperature results where a -63°C change was noted in the 5-second temperature for an exposure of 1.2×10^8R. The impact test results were erratic. If the material had changed, these results are not surprising. Since a detonation velocity could not be achieved, pellets made from BaN_6 were not irradiated. However, in powder form the weight loss for BaN_6 from an exposure of 1.4×10^8R was 4.5%.

According to the DTA traces, the effect of gamma radiation on BaN_6 was significant. As seen in Figure 4 the peak of the exotherm at 210°C for the control sample shifted to 152°C with a total gamma dose of 1.4×10^7R, then to 126°C with a dose of 1.2×10^8R and finally at 1.0×10^9R a very small sharp peak was evident at 265°C.

The thermal stability of BaN_6 was affected by the gamma radiation. The 10% weight loss temperature could not be obtained for any control or irradiated sample at that heating rate. The start of the decomposition was lowered from the control temperature of 193°C to 143°C with an exposure of 1.4×10^7R and further to 100°C for a level of 1.2×10^8R. These samples deflagrated at 133°C, 145°C and 125°C, respectively. The sample exposed to a level of 1.0×10^9R resembled a sample which displayed little reaction - actually only 9.5% weight loss had occurred up to 450°C. The DTA and TGA traces of the 1.0×10^9R sample do resemble those for barium carbonate as shown in the IR spectra.

The IR spectra for BaN_6 indicated that definite shifts had occurred at each increased exposure level from 1.4×10^7R, 1.2×10^8R to 1.05×10^9R. Changes in peaks and intensities are evident as a function of gamma dose but the entire spectra from control to the material subjected to the highest exposure indicated a change in the material. Comparing this to other IR spectra indicated that the 1.05×10^9R BaN_6 became a form of barium carbonate. This is not surprising when it is realized that the BaN_6 was irradiated in air at room temperature for approximately 10^4 hours.

SUMMARY

The effects of gamma radiation on the thermal stability, purity, sensitivity and performance of several military explosives have been determined.

The following threshold limits were derived for damage as a function of total gamma dose:

a. RDX, PETN and NGu can withstand gamma radiation to a level of 1.0×10^7 R.

b. HMX, tetryl, TNB and TNT can withstand gamma radiation to a level of 1.0×10^8 R.

c. TACOT, TATB and DATB can withstand gamma radiation to a level of 1.0×10^9 R.

d. BaN_6 was not able to withstand a gamma radiation level of 1.4×10^7 R.

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REFERENCES

1. L. Avrami, H. J. Jackson, and M. S. Kirshenbaum, "Effects of Gamma Radiation on Selected Fluoroexplosives (U)" PATR 3942 (AFATL-TR-70-29) June 1970 (Confidential Report declassified 27 August 1973).

2. M. S. Kirshenbaum "A Compilation of the Effects of Nuclear Radiation on Explosives of Military Interest (U) PATR 3628, June 1968 (SRD).

3. L. Avrami and W. E. Voreck, "A Determination of Reactor Radiation-Resistant Explosives, Propellants and Related Materials (U)", PATR 3782, November 1969 (C-RD).

4. H. Henkin and R. McGill, "Rates of Explosive Decomposition of Explosives", Ind. Eng. Chem. 44, 1391 (1952).

5. J. Zinn and R. N. Rogers, "Thermal Initiation of Explosives", J. Phys Chem 66, 2646 (1962).

6. T. C. Castorina, J. Haberman, L. Avrami, and E. W. Dalrymple, "Role of Adsorbates During Thermal Initiation of Explosive Decomposition of a Secondary Explosive", Reactivity of Solids, edited by R. W. Roberts and P. Connor, J. Wiley and Sons, Inc., 1969.

7. T. C. Castorina, J. Haberman, E. W. Dalrymple, and A. Smetana, "A Modified Picatinny Arsenal Explosion Temperature Test for Determining Thermal Sensitivity of Explosives Under Controlled Vapor Pressures", Picatinny Arsenal Technical Report 3690, April 1968.

8. H. Rosenwasser, "Effects of Gamma Radiation on Explosives", Oak Ridge National Laboratory Report No. 1720, 6 December 1955.

9. J. V. R. Kaufman, "The Effect of Nuclear Radiation on Explosives", Proc. Roy. Soc. A246, No. 1245, 29 July 1958 (p. 219-225).

10. M. J. Urizar, E. D. Loughran, and L. C. Smith, "The Effects of Nuclear Radiation on Organic Explosives" Explosivstoffe Nr. 3, 1962 (p. 55-64).

11. J. A. Berberet, "The Effects of Nuclear Radiations on Explosive Solid" ATL-TDR-64-53, Air Force Systems Command, USAF (GE-TEMPO Report TMP-37406) 1 January 1965 (Confidential - now declassified).